Published Monthly. Price, $5.00 per Annum.

THE JOURNAL
OF THE
AMERICAN CHEMICAL SOCIETY.

VOL. XVIII.—NO. 3.
MARCH, 1896.

EDWARD HART, Editor, J. H. LONG, THOMAS B. OSBORNE,
COMMITTEE ON PAPERS AND PUBLICATIONS.

CONTENTS.

PAGE.
Third Annual Report of Committee on Atomic Weights. Results Published during 1895. By F. W. Clarke 197
Composition of Wood Gum. By S. W. Johnson 214
Method for the Determination of Carbon in Steel. By Andrew A. Blair 223
A New Safety Distillation Tube for Rapid Work in Nitrogen Determinations. By Cyril G. Hopkins 227
Remarks on Mr. Auchy's Paper on the Volumetric Determination of Manganese. By George C. Stone 228
Probable Production of Permanganate by Direct Combustion of Metallic Manganese. By George C. Stone 230
The Manufacture of Acetone and of Acetone-Chloroform from Acetic Acid. By Edward R. Squibb 231
Pyridine Alkyl Hydroxides. By A. B. Prescott and S. H. Baer 247
On the Reduction of Sulphuric Acid by Copper, as a Function of the Temperature. By Launcelot Andrews 251
The Oxidation of Silver. By Charles E. Wait 254
The Determination of the Solid Fat in Artificial Mixtures of Vegetable and Animal Fats and Oils. By J. H. Wainwright 259
The Measurement of the Colors of Natural Waters. By Allen Hazen 264
Technical Analysis of Asphaltum No. 2. By Laura A. Linton 275
REVIEWS: The Valency of Oxygen and the Structure of Compounds Containing it; The History of Electric Heating Applied to Metallurgy 283
NOTES: The Second International Congress of Applied Chemistry; The Cyanide Method of Extracting Gold from its Ores 307
BOOKS RECEIVED 310

EASTON, PA.:
CHEMICAL PUBLISHING COMPANY.

Entered at the Post Office, Easton, Pa., as Second Class Matter.

Issued with March Number, 1896.

Proceedings.

COUNCIL.

The following persons have been elected as members of the standing committees for one year:

Committee on Papers and Publications—J. H. Long and Thomas B. Osborne.

Committee on Nominations to Membership—A. A. Breneman, P. T. Austen, and C. A. Doremus.

Finance Committee—Durand Woodman, A. P. Hallock, and A. H. Sabin.

C. F. Mabery has been elected a member of the Council for 1896 in place of Charles B. Dudley, President.

The bills of the Chemical Publishing Co. for $289.24 for the January number and $272.43 for the February number of the Journal, have been approved.

NEW MEMBERS ELECTED FEBRUARY 1, 1896.

Bookman, Samuel, 9 East 62nd St., N. Y. City.
Fullam, Frank L., cor. Gold and John Sts., Brooklyn, N. Y.
Hanks, Abbot A., 718 Montgomery St., San Francisco, Cal.
Lihme, I. P., 27 Tift Ave., Cleveland O.
Lippincott, Warren B., 3179 Ashland Ave., Chicago, Ill.
Maywald, F. J., 592 Kosciusko St., Brooklyn, N. Y.
Lerch, Fred., Virginia, St. Louis Co. Minn,
Sharpless, Fred. F., 811 Wright Black, Minneapolis, Minn.
Stearns, F. C., M.D., 44 Montgomery St., Jersey City, N. J.

ASSOCIATE ELECTED FEBRUARY 1, 1896.

Gordon, Alexander, 44 Montgomery St., Jersey City, N. J,

NEW MEMBERS ELECTED FEBRUARY 24, 1896.

Baker, Theodore, Box 97, Belford, N. J.
Barrett, Jesse M., Purdue University, Lafayette, Ind.
Borland, Chas. R., E. C. Powder Co., Oakland, Bergen Co., N.J.
Cheney, John P., So. Manchester, Conn.
Christiansen, H. B., Hermitage, Floyd Co., Ga.
Jones, Wm. J., Jr., Purdue University, Lafayette, Ind.
Martin, Alex. M., F.C.S., Douglas Villa, Dunbeth Road, Coatbridge, Scotland.

Myers, H. Ely, Riddlesburg, Bedford Co., Pa.
Slagle, Robert Lincoln, Brookings, S. D.
Smyth, Dr. Geo. A., 900 South Boulevard, Oak Park, Ill.
Tidball, Walton C., care of E. R. Squibb & Sons, Gold and John streets, Brooklyn, N. Y.

ASSOCIATES ELECTED FEBRUARY 24, 1896.

Pomeroy, Thomas W., Lafayette College, Easton, Pa.
Stover, Edward C., Trenton Potteries Co., Trenton, N. J.

CHANGES OF ADDRESS.

Atkinson, Elizabeth A., Three Tons, Pa.
Baekeland, Leo., care Nepera Chem. Co., Nepera Park, N. Y.
Blalock, Thos. L., 3106 O'Donnell St., Baltimore, Md.
Bromwell, Wm., Ph.D., care Tenn. C. I. and R. Co., 1918–1920 Morris Ave., Birmingham, Ala.
Campbell, Geo. F., 80 Bristol St., New Haven, Conn.
Chamberlain, G. D., care N. W. Mall Iron Co., Milwaukee, Wis.
Cornelison, R. W., care McKenzie Bros. & Hill, Bloomfield, N. J.
Doremus, Dr. C. A., 17 Lexington Ave., N. Y. City.
Foote, Henry B., 241 Walnut St., Cleveland, Ohio.
Graves, W. G., 1661 Huron St., Cleveland, Ohio.
Kenan, Wm. R., Jr., care Carbide Mfg. Co., Box 45, Niagara Falls, N. Y.
Kiefer, H. E., 16 W. 4th St., South Bethlehem, Pa.
Morse, Fred. W., Lock Box 30, Durham, N. H.
Spencer, G. L., Centralia, Wood Co., Wis.
Trubek, M., 325 Academy St., Newark, N. J.
Walker, Henry V., 38–40 Clinton St., Brooklyn, N. Y.

ADDRESS WANTED.

Johnson, Jesse, last address Augusta, Ga.

MEETINGS OF THE SECTIONS.

WASHINGTON SECTION.

The regular monthly meeting of the Washington Section was held December 12, 1895, President Munroe in the chair, with thirty-six members present. In the absence of the Secretary, W. D. Bigelow was elected Secretary, *pro tempore*. The following were elected to membership: W. W. Skinner, F. B. Bomberger, and H. Carrington Bolton. A committee was appointed

to arrange for a social meeting of the Section to report at the January meeting.

The first paper of the evening was "Exhibition of Argon and Helium," by Dr. W. F. Hillebrand. He discussed concisely the spectra of argon and helium and closed by exhibiting the spectra to the Society.

The second paper was by Dr. H. W. Wiley, on the "Use of Acetylene Illumination in Polariscope Work, with Illustrations." Dr. Wiley stated that acetylene, while not inferior in point of accuracy to other forms of illumination, is so intense as to permit accurate polarization with solutions so dark in color that they cannot be polarized with lights commonly used for this purpose. He called attention to the "Schmidt and Haensch Triple Field Polariscope," which was said to be a great assistance in both rapid and accurate work. The paper was illustrated with the acetylene light and the polariscope referred to.

Mr. F. P. Dewey read a paper on "The Early History of Eletric Heating for Metallurgical Purposes." The paper was comprehensive, embracing the various patents relating to electric heating for metallurgical purposes and also many relating to electric reduction. It was illustrated by photographs and drawings of the various forms of apparatus described.

The last paper of the evening was "A Tribute to the Memory of Josiah P. Cooke," by Dr. Marcus Benjamin. An excellent portrait of Prof. Cooke was exhibited and the sketch of his life was of special interest from the fact that the statements made were from a manuscript sent to Dr. Benjamin some years ago by Prof. Cooke. After discussion by Messrs. Munroe, Tassin, and Wiley, the Section adjourned.

NEW YORK SECTION.

The regular meeting of the New York Section was held at the College of the City of New York on Friday evening, Feb. 7, at 8.30 P. M. The following papers were read: New Facts about Calycanthus," by Dr. R. G. Eccles, and "Items of Interest from the Cleveland Meeting," by A. A. Breneman.

Dr. Eccles described his work and also that of Dr. H. W. Wiley on the calycanthus seeds and the alkaloids obtained

therefrom; exhibiting the seeds, the principal alkaloid obtained, its salts, the color reactions of both, and the crystalline forms of the salts.

Prof. Breneman described the features of the Cleveland meeting, which were of particular interest to industrial chemists, referring especially to the low pressure distillation of light petroleum oils as conducted in Prof. Mabery's especially equipped laboratory.

Dr. Durand Woodman exhibited a simple lecture table apparatus for experimentally demonstrating the luminosity of the acetylene flame, generating the gas from calcium carbide.

The meeting was adjourned at 10.45 P. M.

ANNUAL REPORTS OF THE SECTIONS.

The following annual reports from the secretaries of the sections were received by the General Secretary too late for insertion in their proper place:

WASHINGTON SECTION.

Seven meetings have been held and an abstract appended gives the list of papers read and topics discussed at these meetings. The following is a list of the present officers:

President—Charles E. Munroe.

Vice Presidents—E. A. de Schweinitz and W. D. Bigelow.

Treasurer—W. P. Cutter.

Secretary—A. C. Peale.

The officers as above with the following constitute the Executive Committee: H. W. Wiley, F. P. Dewey, F. W. Clarke, and W. H. Seaman. There are no other standing committees.

The secretary of the local section has no way of determining the standing of members. According to a statement made by the General Secretary, December 8, 1894, the membership of the Washington section was sixty-four. As it now appears to be seventy-four the gain during the year is ten.

November 8, 1894.—President W. H. Seaman in the chair. Ten members present. Resignation of Prof. J. C. Gordon read and accepted. Cooperation of the Society asked by John W.

Hoyt in the formation of a "National Post-Graduate University." Prof. H. W. Wiley made a report on the "First Congress ot Chemists," at the San Francisco exposition. Paper read by W. D. Bigelow on the "Coloring-Matter in California Red Wines."

December 13, 1894.—President W. H. Seaman in the chair Twenty members present. Paper by Oma Carr and J. F. Sanborn on the "Dehydration of Viscous Organic Liquids," read by Mr. Carr. Mr. W. D. Bigelow and E. E. Ewell described a continuous extractor for large quantities of material.

January 10, 1895.—President W. H. Seaman in the chair. Fourteen members present. The following officers were elected: President Charles E. Munroe; Vice Presidents, E. A. de Schweinitz and W. D. Bigelow; Treasurer, W. P. Cutter; Secretary, A. C. Peale. Additional members of the Executive Committee, H. W. Wiley, F. P. Dewey, F. W. Clarke, and W. H. Seaman. H. C. Sherman, F. P. Veitch, W. G. Brown, and V. K. Chesnut were elected to membership.

February 14, 1895.—The meeting was devoted to the annual address of the retiring president, W. H. Seaman, upon "Chemistry in Education." President Charles E. Munroe in the chair, with members of the Society ane invited guests from the Societies of Washington present.

March 14, 1895.—President Charles E. Munroe in the chair. Thirty-five members present. Dr. J. E. Blomén and G. E. Barton elected to membership. The following papers were read: "The Constitution of the Silicates," by F. W. Clarke. "On the Chloronitrites of Phosphorus and the Metaphosphinic Acids," by Dr. H. N. Stokes; "The Manufacture of Soluble Nitrocellulose for Nitrogelatin and Plastic Dynamite," by Dr. J. E. Blomén.

April 11, 1895.—President Charles E. Munroe in the chair. Fifty-three members present. The following papers were read: "The Determination of Nitrogen in Fertilizers," by H. C. Sherman; "Exhibition of Calcium Carbide," by Charles E. Munroe; "Precipitation of Small Quantities of Phosphoric Acid by Ammoniacal Citrate of Magnesia," by E. G. Runyan and H. W. Wiley. The Subject for discussion was "Can Argon be Accepted

as a New Element?" Discussion was by Charles E. Munroe, F. W. Clarke, T. M. Chatard, and H. N. Stokes.

May 9, 1895.—President Charles E. Munroe in the chair. Forty members present. Messrs. Marion Dorset and S. C. Miller elected to membership. The following papers were read: "A New Meteorite from Forsyth Co., N. C.," by E. A. de Schweinitz; "Hydrogen Fluoride Poisoning," by Peter Fireman; "Progress in the Manufacture of Artificial Musk," by W. H. Seaman. The subject for discussion was "The Chemical Action of Micro-organisms," and was participated in by E. A. de Schweinitz, Surgeon-General Sternberg, H. W. Wiley, Prof. George P. Merrill, and R. B. Warder.

The Society adjourned until November.

CINCINNATI SECTION.

The annual election held December 18th, 1894, resulted as follows:

President, Karl Langenbeck; Vice-Presidents, B. D. Westenfelder and I. J. Smith; Treasurer, Henry B. Foote; Secretary, E. C. Wallace; Directors, Dr. S. P. Kramer, Prof. O. W. Martin, H. L. Nickel.

The following were elected chairmen of the standing committees for the year:

Didactic, Physical, and Inorganic Chemistry, Dr. Alfred Springer.

2. Organic Chemistry, Prof. T. H. Norton.

3. Analytical Chemistry, Lewis William Hoffmann.

4. Medical, Physiological, and Biological Chemistry, Dr. S. P. Kramer.

5. Technical and Pharmaceutical Chemistry, Prof. J. U. Lloyd.

The following named persons have been elected members of this Section since October 31, 1894: W. G. Wallace, Richard W. Proctor, Charles E. Jackson and George F. Feid, elected December 18, 1894; F. Homburg, E. D. Frohman, elected January 15, 1895; Harry L. Lowenstein, elected Febuary 15, 1895; Prof. A. F. Linn, and Dr. John McCrae, elected October 15, 1895.

In the death of Lewis William Hoffmann and W. G. Wallace

the Cincinnati Section sustained a loss of two of its popular younger members, who were highly esteemed by their associates.

Eight meetings were held during the year, at which the following papers were presented. Special meeting held November 7, 1894, addressed by Dr. H. Hensoldt. The subject announced, "Occult Science in the Orient."

Stated meeting December 18, 1894: "Diphtheria Antitoxin," Dr. S. P. Kramer; "Elective Fermentation in Diabetes," Dr. Alfred Springer.

Stated meeting January 15, 1895: "Separation of the Solid and Liquid Fatty Acids," E. Twitchell; "Report of Progress in Organic Chemistry," Dr. H. E. Newman.

Stated meeting February 15, 1895: Papers announced were postponed on account of sickness of the essayists. "The Difficulty of Obtaining Distilled Water to Meet Pharmacopeial Requirements," was discussed by Prof. Lloyd, Dr. Springer, and Prof. Norton.

Stated meeting March 15, 1895: "Determination of Phosphorus in Ferrosilicon," John H. Westenhoff; "The Souring of Milk," Robert W. Hochstetter.

Meeting April 16, 1895: "Recent Important Discoveries in Chemistry," Prof. T. H. Norton.

Meeting May 15, 1895: "Adulteration of Powdered Elm Bark," Henry B. Foote; "Ammonium Thioacetate," Prof. T. H. Norton.

Stated meeting October 15, 1895: "A Tribute to Pasteur," Dr. Alfred Springer; "Laboratory Uses of Aluminum and Recent Progress in Theoretical Chemistry," Prof. T. H. Norton.

A pamphlet issued by the Executive Committee gives names, occupation and addresses of members of the Section, the names of the authors and titles of papers read during 1894.

NEBRASKA SECTION.

The Nebraska Section was organized at a meeting held in Lincoln, June 14, at which meeting officers were elected for the ensuing year, as follows:

President, H. H. Nicholson; Secretary and Treasurer, John

White; Executive Committee, H. H. Nicholson, John White, Rosa Bouton, T. L. Lyon, W. S. Robinson.

The first regulnr meeting of the Section was held in the Chemical Laboratory of the University of Nebraska on October 30, with a good attendance of members and a number of invited guests.

Papers were read as follows:

By Prof. T. L. Lyon: "The Source of Error in the Estimation of Sugar in Beet Juice by Means of the Sucrose Pipette."

By Mr. Samuel Avery: "Notes on the Electrolytic Determination of Iron, Nickel and Zinc."

Mr. C. H. Suveau, of the Department of Motive Power of the Burlington and Missouri River Railroad, was elected a local associate member.

Other meetings will be held in December, March and June.

Our present membership is thirteen.

CHICAGO SECTION.

The Chicago Section has held but two meetings, one for organization, and the other just reported, at which papers were presented.

The membership is twenty-five.

The officers are as follows:

President, Frank Julian; Vice-President, J. C. Foye; Secretary, F. B. Dains; Treasurer, J. H. Long; Executive Committee, Frank Julian, A. L. Smith, F. B. Dains.

NEW YORK SECTION.

Meetings were held and papers read as follows:

November 9, 1894: "The Rapid and Accurate Analysis of Bone-black," by William D. Horne; "Recent Progress in Physiological Chemistry," by Dr. E. E. Smith.

December 13, 1894: The Chemical Nature of Diastase," by Thomas B. Osborne, of New Haven; "Glucose from a Sanitary Standpoint," by E. H. Bartley, M.D.; "Indiscriminate Taking," by P. T. Austen.

January 10, 1895: "Improvement in the Manufacture of Acetone," by Dr. E. R. Squibb; "Recent Progress in Photographic Chemistry," by Dr. J. H. Stebbins.

February 18, 1895: No quorum.

March 8, 1895: "The Late Prof. Henry B. Nason," by W. P. Mason; "Elective Fermentation in Diabetes," by Alfred Springer; "Note on Absorbent Blocks," by W. H. Broadhurst; "Note on the Precipitation of Iron by Alkali Nitrites," by Gillett Wynkoop; "Volumetric Determination of Zinc and Manganese and a New Indicator for Ferrocyanides," by G. C. Stone; "Note on the Reduction of Nitrates by Ferrous Hydroxide," by P. T. Austen; "Stability to Light of Haematoxylin Blacks on Wool," by P. T. Austen.

May 11, 1895: "Recent Progress in Analysis of Soils," by H. W. Wiley; "Tribute to the Memory of Dr. Gideon Moore," by C. F. McKenna; "Chemical History of Caase of Arsenical and Antimonial Poisoning," by C. A. Doremus; "The Estimation of Acetic Acid in Vinegar," by A. R. Leeds.

June 14, 1895: "Determination of Nitrogen by the Gunning Method," by W. D. Field; "On Asbestos and its Commercial Application," by G. C. Stone; "Examination of Lard for Impurities," by David Wesson; "On Commercial Argol and its Products," by Wm. McMurtrie; "A Modern View of Electro-Chemical Action," by C. L. Speyers; "On the Relation of the Chemical Engineer to Factory Management," by John Enequist.

The informal dinners preceding the meetings have been continued at a majority of the meetings. The total expenditures of the section have amounted to $157.98; those of the preceding year were $160.82. The largest item in each case is the contribution to the Treasury of the Scientific Alliance.

The following officers have been elected for the current year; Chairman, P. T. Austen; Secretary and Treasurer, Durand Woodman; Executive Committee, A. H. Sabin, A. C. Hale, A. R. Leeds; Delegates to Council of Scientific Alliance, P. T. Austen, C. F. McKenna, A. C. Hale.

The list of members is annexed hereto, and shows a total membership of 234 as compared with 183 last year, or a gain of fifty-one members.

RHODE ISLAND SECTION.

The Rhode Island Section of the American Chemical Society

respectfully transmits the following general report of the business of the Section for the year September 1, 1894, to September 1, 1895.

The work of the Rhode Island Section for the past year may be described in brief as follows, all the meetings having been held in Providence :

September 27, 1894 : A paper prepared by Prof. E. E. Calder upon the " Chemistry of Albuminurea," was read by Mr. W. M. Saunders, the author being unable to be present.

October 18, 1894 : A paper was read by Mr. W. M. Saunders upon " Lantern Slides and their Preparation," illustrated by the stereopticon.

December 13, 1894 : A paper was read by Charles A. Catlin, upon " Bread and Bread Stuffs."

January 17, 1895 : A paper was read by Mr. Geo. F. Andrews upon " The Accuracy of the fire assay of Silver."

February 23, 1895 : A paper was read by Prof. J. H. Appleton upon " Argon."

March 21, 1895 : A paper was read by Mr. J. P. Farnsworth upon " Selection of water for Bleaching and other Manufacturing Purposes."

April 24, 1895 : A paper was read by Mr. C. H. Burgess upon " A Resumé of the methods of Bleaching Cotton Piece Goods."

May 23, 1895 : A paper was read by Mr. E. D. Pearce upon " The Coloring-Matter of Pollens," with illustrations under the microscope.

June 13, 1895 : The annual meeting was held at the Hope Club House where the members were entertained at dinner as the guests of the Chairman, Mr. Charles A. Catlin, who presented a paper upon " Chemical-Laboratory Microscopy," illustrated by the microscope.

The interest in the local section still continues to be well sustained, and already another new year of its work has begun with very flattering prospects for the future.

At present date the names of the officers of the Section are : Chairman, Charles A. Catlin ; Secretary and Treasurer, Walter M. Saunders ; Executive Committee, Chairman, ex-officio, Secretary and Treasurer ex-officio, George F. Andrews.

Number of members belonging to the Rhode Island Section at the present time, twenty (20). Net increase over last year two (2).

LEHIGH VALLEY SECTION.

It has been found desirable, as the Section is limited in number, to hold fewer meetings. Four meetings have been held during the past year; *viz.*, November 1, 1894, January 17, May 2, and October 10, 1895. The October meeting was the most successful in the history of the Section, the Society entertaining at that time Thomas Tyrer, Esq., President of the Society of Chemical Industry of England, and invited representatives of the New York Section of the same Society and the New York Section of the American Chemical Society. An inspection of the large government plant of the Bethlehem Iron Co. was made, followed by an elegant dinner tendered the visiting chemists, while the stated meeting was held in the afternoon at Lehigh University.

The following papers have been presented: "Helmholz's Contributions to Science," George P. Scholl; "Castner's Electrolytic Process for Production of Caustic Soda," W. H Chandler; "A New Ammonia Condenser," Edward Hart: "The Determination of Graphite in Pig Iron," P. W. Shimer; "The Selection of Samples for Analysis," A. L. Colby; "On standardization of Iodine Solution," G. H. Meeker; "A Device for Sampling Metals," P. W. Shimer; "The Rapid Methods Used in the Bethlehem Iron Co.'s Laboratory," A. L. Colby.

Mention should also be made of the interesting paper read by Dr. William McMurtrie at the October meeting, on "Chemical vs. Bacteriological Examination of Water," written by Prof. W. P. Mason.

We close the year with the same number as we began, *viz.*, 21, losses having been made up by new members.

Our annual meeting will be held the third Thursday in January. The officers of the Section for the year 1895 are as follows:

Presiding Officer—Edward Hart.

Treasurer—Albert L. Colby.

Secretary—Albert H. Welles.

Executive Committee—Edward Hart, Albert L. Colby, Albert H. Welles, and J. W. Richards.

THE CLEVELAND EXCURSIONS.

Owing to delay in the receipt of copy it was impossible to give a full account of the meeting at Cleveland in last month's issue. The following additional matter has since been received by the editor:

One very pleasing feature of the meeting in Cleveland was the excursions to various works and other places of interest. Both afternoons were set apart for this purpose, one special party made a trip on Tuesday morning, and on Monday evening the Case School of Applied Science and Adelbert College were visited. Such a large number of excursions were planned, and so many works were freely opened for inspection, that it was impossible to visit them all. Routes Nos. 1, 6, and 7, as given by the local committee's program, were omitted, and all the time available was devoted to the others.

Route No. 2 was led by Mr. D. B. Cleveland, chemist of the American Wire Works.

The first place visited was the plant of the Otis Steel Co. Mr. Bartol, the Superintendent, took charge of the visitors and showed them the plate mill, the basic open hearth furnaces, the steel foundry, the car axle foundry, the machine shop and the laboratory.

The Continental Chemical Co. was next visited. They make red pigments and fuming sulphuric acid from copperas, but had unfortunately been recently burned out, so that it was impossible to see the works.

The manager, Dr. Ramage, exhibited an apparatus for making ozone, which he said brought its cost down to such a point as to warrant its being used for disinfecting garbage, refuse from stock-yards, fats, etc.; for bleaching, for oxidizing sulphurous to sulphuric oxide, thus doing away with the lead chambers in the manufacture of sulphuric acid, and for many other purposes.

He claimed that treatment with ozone is an almost sure cure for consumption in the first two stages and for syphilitic diseases.

He stated that with one-fifth to one-seventh of a horse power he can change one hundred and twenty cubic feet of atmospheric air a minute to a mixture containing fifteen to eighteen per cent. of ozone, all the oxygen present being changed. He uses a fifty volt and two to three ampere alternating current, which he converts to a current of fifty thousands volts.

The Cleveland Nitrous Oxide Co. was next visited, and Mr. Clark and Mr. Hatch showed the party around.

They sell oxygen and hydrogen, epsom salts, liquid nitrous oxide and carbonic acid gas. They also make nitrate of ammonia, as the commercial salts is to impure for their use.

They exhibited some acetylene gas burning from an ordinary gas jet to show the character and illuminating power of this much talked-of new illuminant.

By this time it was too late to visit other places of interest, and the party returned to the hotel.

Route No. 3 was taken on Tuesday morning, the members of this party thus missing the regular morning session. This was done at the suggestion of the Managers of the Varnish works, as their work of boiling varnish could only be seen in the morning. The party was guided by Mr. George Marshall, and included the following places: Cleveland Varnish Co., Cleveland Rubber Co., Glidden Varnish Co., and Warner & Swasey, instrument makers.

A party of six started Tuesday at 9 A. M. from the Hollenden and proceeded to the Cleveland Varnish Co., where Mr. Stark, the chemist, conducted them through the works and explained the different processes. The store-room was first visited, wherein large boxes of rosin are stored, some from New Zealand and some from Zanzibar, the first-named place being the chief source. The gums or rosins used for varnish are amber, fossil and annual; amber and fossil are best, as the thousands of years they have lain in the ground seems to have cured them. These gums are assorted according to color, the lightest being the most valuable. They are found by probing in the sand, in lumps from the size of a bean to that of a wash tub. The largest piece of Kauri gum found weighs 250 pounds. This is the chief gum, but Zanzibar is also used for fine varnishes. These gums are insoluble

in common solvents or oil, and must be melted at 560° F. in order to decompose partially, so that they may unite with the oil. The chemists visited the boilers where the operation of dissolving the gum was in progress. These boilers are large vessels, in shape somewhat like the farmer's sap or soap kettles, placed on a small buggy to facilitate removal from the fire. From twenty to twenty-five per cent. is driven off as water and non-drying oils on heating. The latter are unstable, and have not been investigated or utilized, except in connection with the lampblack industry. The gums are prepared for the boilers by hand, as the best size for melting (about that of a hen's egg), is obtained by chopping with a small hatchet. The machines crush them too fine. Linseed oil does not dry quickly unless boiled, and dryers are made by adding a lead or manganese salt to boiled oil. These combine with the oil, forming a compound which absorbs oxygen quickly and hardens. The boilers for oil are the same as for melting, generally larger, with hoods to carry off volatile products. The gum boilers are fitted with covers to decrease loss from spattering and to control the irritating fumes which are carried off by means of tall chimneys. Different solvents, as turpentine, for instance, are used to give required consistency to the finished varnish, and are added to the cooled mixture formed by adding boiled oil to the melted gum. The varnish is then allowed to settle in large tanks for from two months to as many years. The longer the time the finer the varnish made. This is necessary, as filtering does not remove the sediments. The top is siphoned off, filtered through filter presses and run into tanks for ageing. The ageing room is kept at a constant temperature, such that the varnish is fluid for from nine to eleven months. The party visited the cooper shop, storage tanks, shellac mixers, (which are nothing more than a barrel fastened on a shaft to rotate in the direction of its circumference), and a paint mill of the latest pattern, which does not materially differ from the earliest ones made. The filters were of the well known Johnson's make, and the cloths may be used one day, then removed and agitated in a shellac mixer with turpentine until the gummy sediment is washed out. Each lot of varnish, japan, or enamel after ageing

is tried, *i. e.*, some substance for which it will eventually be used as a cover, is coated with it and dried or baked.

The most noticeable feature at the Varnish Co., sets aside the old adage about the shoemaker's wife and blacksmith's colt, for paint and varnish had been used in a very neat and tasty manner throughout the establishment, and what was particularly prominent, was the absolute cleanliness that pervaded even the store-rooms, the settling and ageing rooms where long lines of tastefully painted tanks pleased the eye, and the excellent arrangement of drafts, hoods, covers and stacks to carry off the offensive odors detrimental to the workman's health.

After visiting the laboratories and drying rooms, the offices were next in order, where a most pleasant surprise was in store. At the invitation of the president, Mr. Tyler, the chemists sat down to a most elaborate luncheon, which was very acceptable. After a vote of thanks had been given their hospitable host, the visitors wended their way to the Cleveland Rubber Co.

Notwithstanding the torn up condition of the rubber company on account of inventory, every courtesy was shown by the foreman of each department, who personally explained his part of the work. The first room visited was the calendering room, where the crude exudings of the South American rubber trees are mangled into workable shape. The rubber gum as received contains fourteen to eighteen per cent. water, and ten to twelve per cent. extraneous matter, such as stones, twigs, bark, etc. Stones are the favorite adulterants, as the crude gum is bought by weight. The gum is first run through rollers upon which water plays, to cleanse it. It comes from the rollers looking like a sheet of thin cork. It is then allowed to cure for three or four months in a dry room at about 70° F. The South American natives cure rubber by exposure to air and sun, so that vulcanization is not necessary, and they make very durable shoes from the product so cured. Modern science has not yet perfected a system for hastening this curing operation, and it is necessary to cure at 70° three or four months since higher heat has a decomposing effect. From the curing room the rubber is passed through slightly heated rollers again and again until it becomes a compact, yielding, non-porous mass. A little vaseline added

in this working serves to make the mass more pliable and softens it. From the first rollers it passes to others, where different colored powders are added and worked into the body of the rubber. Pure rubber is black and is useless for many purposes, but by mixing with various constituents it may be impressed into the pores of cloth, making a covering impervious to moisture, rolled into sheets capable of holding gases or liquids, moulded into any shape, hardened by heat, and welded. The fillers, as they are called, are zinc oxide, whiting, lampblack, litharge, sulphide of iron and antimony, and many other substances known only to the trade. Each filler has a different effect on the rubber. Sulphide of antimony is used for fine elastic rubber, such as is used in dental operations and for marine valves. In general, if rubber is to be hardened, as when used for door mats, or if the surface is made impervious to moisture or air for gas bags, water bottles, mackintoshes, hose, bicycle tires, etc., sulphides are used in order that vulcanization may take place after the article is formed. Litharge, lampblack and zinc oxide give color as well as body to the rubber. In order to cover cloth the rubber is wound on rollers and fed through calenders or heated rolls set to such a size that rubber introduced between the rolls in mass is forced through the cloth and becomes part of it; at the same time, by heating the rolls vulcanization also takes place. Vulcanization consists of forming a compound of sulphur and rubber in air by heating, and although it takes much of the elasticity from the rubber, renders it impervious to liquids or gases. Cloth was shown prepared in this way for mackintoshes, hose, etc. Cloth so prepared may be sewed together; a solution of rubber in any volatile solvent applied to the stitches, or the seam covered with a strip of rubber wet with this solution, the whole placed in a steam-heated oven, heated and when withdrawn it is found the cement has welded the holes left by stitches, or the strip upon the original pieces so that it becomes a compact mass.

The party next visited the molding department. Here the rubber is prepared as above with a filler of some sulphide and then pressed like dough into heated molds. It is very plastic, filling all crevices readily and taking every impression. It does

not melt, but first heat softens it to the consistency of soft taffy, while a greater heat vulcanizes it. In order to keep surfaces in contact from welding together, a little whiting is sprinkled between them. Scraps are reworked, and old rubber, such as boots, is reclaimed and made into coarse articles, such as mats. The mechanical arrangements were (some of them) wonderful, but space cannot be given to a detailed description of them all. As the time for the morning excursion had now been expended, the party were obliged to forego the pleasure of visiting the other places of interest on the list.

It is to be regretted that more did not avail themselves of the opportunity extended to them to visit these works.

Route No. 4 was for convenience, divided into two excursions, the Grasselli Chemical Works being visited on Tuesday and the other places on Monday.

The trip to the Oil works was under the guidance of Mr. H. L. Payne, chemical engineer, and the visitors were introduced to the practical side of a subject, whose chemical side was so interestingly presented by Dr. Mabery in his address on the same evening. Only one refinery was visited.

The one selected is not under the control of the Standard Oil Co., and works up all of its own product. The visitors were therefore fortunate in being able to see within the confines of one muddy hillside all the branches of this vast industry. The members of this firm, Messrs. Scofield, Shurmer & Teagel, were all very obliging, and Mr. Daniel Shurmer and his son personally conducted the party through the extensive works.

The stills are sheet steel tanks set in brick work and have an open coal fire under them. Some are set on end and others lie on the side. They are not usually covered in like a boiler, but exposed to the air on top and sides, and only protected from the weather by a rough shed. This circumstance would seem to cause a waste of fuel, but it probably assists in the proper "cracking" of the oil. The distillate is condenced in a series of wrought iron pipes, which are kept cool by immersion in a long wooden trough. The trough is kept filled with cold water from springs in the side hills. Various methods of procedure are adopted in the distillation, depending upon the character of

the product desired, for not all of the various oil products are or can be made in one distillation. The lighter and more volatile products are usually collected together and then redistilled with steam heat in order to separate them into commercial "naphtha," "benzine," "gasoline," etc. In this distillation the steam is introduced directly into the oil and the condensed water is drawn off at the bottom of the still-tank. The very light vapors and gases which come off first are sucked down by a steam syphon and burned under the boilers.

The residue left in the crude oil stills may be either a thick tarry pitch or the distillation can be carried so far that only a porous coke is left. This coke contains only 0.01 to 0.02 per cent. ash, and is in great demand for the manufacture of electric-light carbons.

The burning oils are all purified by washing in a huge lead-lined separatory funnel, called an agitator. They are first washed with concentrated sulphuric acid which unites with and precipitates the basic matters, such as phenol. The oil after this washing contains less oxygen than before. The principal object of this treatment is to remove those bodies which would cause a coloration of the oil; a water-white kerosene is supposed to best suit the consumer. The excess of acid is washed out with water or steam and the oil is completely neutrallized by a little caustic soda. The refinery is using some Lima oil, and they treat it with litharge in the agitator to remove the sulphur. Other refineries use copper oxide in their stills for the same purpose.

One of the most interesting products of crude oil is paraffin. It distills over as a greenish oil, and the visitors were permitted to examine the crystallizing process where the solid wax is frozen out and filtered from the more liquid part of the oil. A second or third tereatment of the crude wax with solvent naphtha and this freezing process, turns out the pure white chewing gum. Every paraffin works has its own ammonia freezing plant.

Most of the refineries have no chemist in their employ. They are mainly concerned with the physical properties of their products, and a boy soon learns to make the test for specific gravity, flashing point, burning point, freezing point and viscosity.

The cooperage and shipping departments were large and interesting, but when the party arrived at that portion of the works they were ready to return to the hotel.

The other excursion of Route No. 4 was taken by all on Tuesday morning. The Grasselli Company's works are of such magnitude that a description is impossible. They make sulphuric acid, nitric acid, hydrochloric acid, mixed acid for nitroglycerol factories, ammonia, glycerol, and all the various salts and bye products of such an industry. Mr. E. F. Cone, chief chemist of the experimental laboratory, was the conductor on this occassion, and Mr. C. A. Grasselli, president, and his staff of superintendents were instrumental in showing everything in the works. None of the chemists will forget the pleasant little lunch which awaited them in the company's office.

Route No. 5 was of interest to iron works chemists, and comprised the Cleveland Rolling Mill and the Blast Furnace department and mill of the Union Rolling Mill Co. It was in charge of Mr. F. E. Hall.

The party left the Square at 1:30 P.M. Monday and proceeded first to the Cresent Sheet and Tin Plate Co.'s Works on Bessemer Avenue, near the N. Y. P. & O. R. R. This company employs two hundred men and has a capacity of thirty tons per day of sheet iron and tin plate. The plant is new, having been in operation about one year, and is fitted up with all the latest improvements in boilers, engines and all machinery, including an electric plant for lighting, and operating the electric cranes for handling rolls and heavy materials.

From here the party proceeded to the Emma Blast Furnace at the intersection of the N. Y. P. & O. and C. & P. Railroads. This furnace is operated by the Union Rolling Mill Co., whose rolling mills were visited later. The furnace department employs one hundred men and has a capacity of two hundred tons of pig iron daily. The plant is modern in every respect, has three blowing engines and three brick hot blast stoves. The company's chemical laboratory is located at the furnace plant and is in charge of Mr. Frank E. Hall.

The next place visited was the rolling mill of the same company, situated some distance farther up the C. & P. R. R. Here

are employed about 350 men, the daily produced of the works being about 150 tons of merchant iron. No steel is made, the company making a speciality of high grade wrought iron.

After inspecting this plant the party proceeded to the large works of the Cleveland Rolling Mill Co. This works is the largest in the city. The Bessemer Steel plant has a capacity of 1,000 tons daily, about seventy-five per cent. of which is made up into finished products, consisting of rails, shafts and wire, in the various departments of the company's works. In all about 3,500 men are employed.

One blast furnace is located at this plant. The company's two larger furnaces are located about three miles farther down on the N. Y. P. & O. R. R., from which place "direct metal" is run to the converters, the molten metal being carried this distance over the N. Y. P. & O. R. R.

The chemical laboratories of the company are in charge of Mr. Chaddock. Ten chemists are employed.

Route No. 8, Adelbert College and Case School of Applied Science were appointed for Monday evening. Dr. Gruener, instructor of chemistry in Adelbert College, was absent on his vacation, and Mr. H. L. Payne, a graduate of the first chemistry class in Case School, was appointed to head this excursion.

The new physical laboratory of Adelbert College exicited the greatest admiration. The chemical laboratory lacked its most interesting feature—Dr. E. W. Morley.

At Case School the visitors saw the marks of an active and well equipped institution for the study of practical applied science. The entertainment of the evening, of course, was Dr. Mabery's talk on "Petroleum."

Route No. 9 was to the Steel Works at Lorain, O. The trip was in charge of Mr. Hugo Carlsson, chief chemist of the Johnson Co.

These works occupy about eighty-six acres of land lying along the Black river, two miles south of Lorain. The plant was first put in operation April 1, 1895. Their finished products are billets and special rails for street railways. The plant consists of the Bessemer department, blooming mill, shape mill, engine and boiler houses, etc. Plans for the erection of six blast fur-

naces have been completed and work will begin on the erection soon.

The engine house contains the blowing engine for the Bessemer department; this was made by the Southwark Company, Philadelphia. It is a horizontal double expansion engine with blowing cylinder sixty inches diameter and sixty inches stroke. In the same building are the dynamos and straight line engines which furnish power for the Johnson Electric Railway between Lorain and Elyria. There are two boiler houses containing National Water Tube Boilers with Murphy Automatic Stokers, the combined capacity of the two batteries being about 6,000 horse power. The feed water is heated and purified before it enters the boilers. Gas for the heating furnaces is furnished by a plant of Duff gas producers. Four ten-foot cupolas melt the pig metal, and there are two eight-foot cupolas for spiegel. The converting department contains two ten ton vessels. Ingot molds are arranged on small cars in pairs. There is no casting pit. The ingots are transferred from the converter house to the soaking pits, in which they are kept until ready for rolling. The blooming mill is driven by a very powerful reversing engine, built by the Galloways, Manchester, England. It has double cylinders each fifty-five by sixty inches. The shape mill is driven by two engines, also of the Galloways' make. The heating furnaces are provided with two cranes, one for charging and one for drawing.

An important feature of the works is the special machinery for straightening rails. The laboratory occupies a two-story brick building, and contains a 250,000 pound Olsen testing machine.

THE RECEPTION BY THE CHAMBER OF COMMERCE.

The various hosts who had vied with one another in extending courtesies and hospitalities to the visiting chemists while in Cleveland, not being satisfied with the royal welcome which they had already given, tendered their guests a most delightful reception in the rooms of the Chamber of Commerce, Tuesday evening, Dec. 31. We quote from a Cleveland paper the following description of the elaborate decoration of the rooms:

"The decorations were to a certain extent paradoxical, being

emblematic of both summer and winter. The walls of the ceiling were draped with holly, heavily laden with red berries. This drapery came down to within a few feet of the floor, where it was met by banks and screens of palms and other tropical plants. This apparent paradox was a pretty tribute to the various sections of the country, north and south, from which the guests came.

The floral designs added to the beauty of the scene. One, a large shield of white, studded with roses, bore the following inscription:

'Welcome, 1895—American Chemical Society.'

In the center of the assembly room, on a table, stood an immense design which was a tribute to Dr. E. W. Morley and took the form of a reference to his great genius in determining the atomic weight of oxygen. It was a huge balance erected on a base of American beauty roses. From the arms of the balance hung globes of white flowers. On one in purple was the simple capital letter 'O,' representing oxygen, and on the other the purple figures '15.879,' the atomic weight of oxygen."

On entering the Chamber the guests were welcomed by the Reception Committee, and introduced to the Cleveland gentlemen who were present. From early in the evening until midnight the visiting chemists had the pleasure of meeting in social intercourse those who had already done everything in their power to welcome and entertain the American Chemical Society, and to furnish them opportunities for a successful meeting.

During the evening the Chamber of Commerce Musical Club and the Schubert Mandolin Club rendered various choice selections, which were enthusiastically received. The evening was also enlivened by the humorous recitations and impersonations of Mr. J. E. V. Cooke.

Refreshments were served during the evening in the committee room, and it seemed as though nothing was wanting to make the occassion one long to be remembered. To cap the climax, however, and to show their appreciation of one of Cleveland's most distinguished scientists, a message of greeting and complimentary reference to his labors in determining the atomic weight of oxygen, was sent by cable to Dr. E. W. Morley, who is spending the winter in Europe.

Some of the chemists were obliged to leave on early trains and were thus unable to enjoy the whole of the evening. But they, as well as those who remained, took with them the pleasantest recollections of their visit to Cleveland, and the Twelfth General Meeting of the American Chemical Society.

Erratum.—Page 32, sixth line from bottom of page *for* sixty-three per cent. *read* sixty-three hundredths of one per cent.

VOL. XVIII. [MARCH, 1896.] NO. 3.

THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY.

THIRD ANNUAL REPORT OF COMMITTEE ON ATOMIC WEIGHTS. RESULTS PUBLISHED DURING 1895.[1]

BY F. W. CLARKE.

Received January 3, 1896.

To the Members of the American Chemical Society:

YOUR committee upon atomic weighis respectfully submits the following report, summarizing the work done in this branch of chemistry during 1895, a year which may be well called eventful in the history of the science. Two new elements, argon and helium, have been made known to the world, and from the most unexpected sources; the collective works of Stas have been published by the Belgian Academy, as a monument to his memory; Prof. Morley's great research upon oxygen is at last finished; and a goodly number of other important determinations have appeared. Incidentally, but pertinently, I may also call attention to the Marignac memorial lecture by Cleve,[2] in which the atomic weight researches of the former chemist are well outlined; and to the extraordinary number of papers upon the periodic law, which have been called out by the discovery of argon and helium. These papers fall outside the scope of this report, and they are numerous enough to almost warrant a bibliography of their own.

The H : O ratio.—Prof. Morley's work upon this fundamental constant has been published in full by the Smithsonian Insti-

[1] Read at the Cleveland Meeting, December 31, 1895.

[2] *J. Chem. Soc.*, June, 1895.

tute,[1] and divides itself naturally into four parts: First, the density of oxygen; second, that of hydrogen; third, the volumetric composition of water; and fourth, its gravimetric synthesis.

For the density of oxygen, or rather the weight of one liter at 0°, 760 mm., at sea level and in latitude 45°, three sets of measurements are given, with the following mean values in grams:

Series	1	1.42879 ± 0.000034
"	2	1.42887 ± 0.000048
"	3	1.42917 ± 0.000048

As the third series, on experimental grounds, is regarded by Morley as the best, he assigns it double weight, and on this basis the general mean of all three becomes

$$1.42900 \pm 0.000034.$$

For the weight of a liter of hydrogen, under similar standard conditions, five series of determinaiions are given, as follows:

Series	1	0.089938
"	2	0.089970
"	3	0.089886 ± 0.0000049
"	4	0.089880 ± 0.0000088
"	5	0.089866 ± 0.0000034

The hydrogen of the first and second series was probably contaminated by traces of mercurial vapor, and these results are therefore rejected by Morley. For the third, fourth and fifth series the electrolytic gas was occluded in palladium and transferred to the measuring globes without the intervention of stop-cocks; thus avoiding contact with mercury and leakages of external air. Their general mean is

$$0.089873 \pm 0.0000027.$$

Dividing the weight found for oxygen by this value for hydrogen the ratio becomes

$$15.9002.$$

For the volumetric ratio O : 2H, Morley finds the value

[1] "On the densities of Oxygen and Hydrogen, and on the Ratio of their Atomic Weights." By Edward W. Morley. Smithsonian Contributions to Knowledge, 1895. 4to. xi + 117 pp. 40 cuts. Abstract in *Am. Chem. J.*, 17, 267, (gravimetric); and *Ztschr. phys. Chem.*, 17, 87, (gaseous densities); also note in *Am. Chem. J.*, 17, 396.

1 : 2.00269. Applying this as a correction to the density ratio, we have for the atomic weight of oxygen

$$O = 15.879.$$

In his synthesis of water Morley differs from all of his predecessors in that he weighed both constituents separately, and also the water formed. In other words, his syntheses are complete, and take nothing for granted. The weights in gram are as follows:

	O used.	H used.	Water found.
1	25.9176	3.2645	29.1788
2	25.8531	3.2559	29.1052
3	30.3210	3.8193	34.1389
4	30.5294	3.8450	Lost.
5	30.4700	3.8382	34.3151
6	30.5818	3.8523	34.4327
7	30.4013	3.8297	34.2284
8	30.3966	3.8286	34.2261
9	30.3497	3.8225	34.1742
10	30.3479	3.8220	34.1743
11	29.8865	3.7637	33.6540
12	30.3429	3.8211	34.1559

From these data, two sets of values for the atomic weight of oxygen are derivable; one from the ratio H : O, the other from the ratio H : H_2O. These sets are subjoined.

	H : O.	H : H_2O.
1	15.878	15.877
2	15.881	15.878
3	15.878	15.873
4	15.880	.....
5	15.877	15.881
6	15.877	15.876
7	15.877	15.875
8	15.878	15.879
9	15.879	15.881
10	15.881	15.883
11	15.881	15.883
12	15.882	15.878
Mean	15.8792	15.8785

From the density work the value found was 15.879, and the mean of this with the two synthetic results is

$$O = 15.8789.$$

Hence, for all practical purposes, the atomic weight of oxygen may be put at 15.88, with an uncertainty of less than one unit in the second decimal.

It is impracticable, in a report of this kind, to go into the details of so elaborate an investigation as this of Morley's, and a bare statement of results must suffice. The research, however, is one of the most perfect of its kind, every source of error having been considered and guarded against, and it will doubtless take its place in chemical literature as a classic. Independently of its main purpose, the book is almost a manual on the art of weighing and measuring gases, and no experimenter who engages upon work of that kind can afford to overlook it.

More recently still, a new determination of the atomic weight of oxygen has been published by Julius Thomsen,[1] whose method is quite novel. First, aluminum, in weighed quantities, was dissolved in caustic potash solution. In one set of experiments the apparatus was so constructed that the hydrogen evolved was dried and then expelled. The loss of weight of the apparatus gave the weight of the hydrogen so liberated. In the second set of experiments the hydrogen passed into a combustion chamber in which it was burned with oxygen, the water being retained. The increase in weight of this apparatus gave the weight of oxygen so taken up. The two series, reduced to the standard of a unit weight of aluminum, gave the ratio between oxygen and hydrogen.

The results of the two series, reduced to a vacuum and stated as ratios, are as follows:

First, $\frac{\text{Weight of H.}}{\text{Weight of Al.}}$	Second, $\frac{\text{Weight of O.}}{\text{Weight of Al.}}$
First.	Second.
0.11180	0.88788
0.11175	0.88799
0.11194	0.88774
0.11205	0.88779
0.11189	0.88785
0.11200	0.88789
0.11194	0.88798
0.11175	0.88787

[1] *Ztschr. anorg. Chem.*, 11, 14.

First.	Second.
0.11190	0.88773
0.11182	0.08798
0.11204	0.88785
0.11202	
0.11204	0.88787 ± 0.000018
0.11179	
0.11178	
0.11202	
0.11188	
0.11186	
0.11185	
0.11190	
0.11187	

0.11190 ± 0.000015.

Dividing the mean of the second column by the mean of the first, we have for the equivalent of oxygen:

$$\frac{0.88787 \pm 0.000018}{0.11190 \pm 0.000015} = 7.9345 \pm 0.0011.$$

Hence, $O = 15.8690 \pm 0.0022$.

The details of the investigation are somewhat complicated, and involve various corrections which need not be considered here. The results as stated, includes all corrections and is evidently good. The ratios, however, cannot be reversed and used for measuring the atomic weight of aluminum, because the metal employed was not absolutely pure.

The Stas Memorial.—As a monument to the memory of the late Jean Servias Stas, more appropriate than statue or column of stone, the Belgian Academy has published his collected works in three superb quarto volumes.[1] All of his great investigations are here gathered together, and in the third volume, entitled "Oeuvres Posthumes," some hitherto unpublished data are given for the important ratio between potassium chloride and silver. These data are represented by two series: one made with a uniform sample of silver, and chloride from various sources; the other with constant chloride, but with silver of diverse origin; the aim being to establish experimentally the fixed character of each substance. The first series is complete;

[1] Jean Servias Stas. Oeuvres Complétes. Edited by W. Spring. Bruxelles, 1894.

of the second series only one experiment was found recorded among Stas' papers.

The quantity of potassium chloride equivalent to 100 parts of silver was found to be as follows:

	69.1227
	69.1236
	69.1234
	69.1244
	69.1235
	69.1228
	69.1222
	69.1211
	69.1219
	69.1249
	69.1238
	69.1225
	69.1211
Mean of first series	69.1229
Second series	69.1240

These results give an effective confirmation to Stas' determinations of 1882.

Cobalt.—The atomic weight of cobalt has been redetermined by Thiele.[1] First, carefully purified oxide of cobalt, CoO, was reduced in hydrogen. The weight and results are as follows:

Residual Co.	Loss of O.	Atomic weight of Co.
0.90068	0.24429	58.843
0.79159	0.21445	58.912
1.31558	0.35716	58.788
	Mean	58.848

Reduced to vacuum standards this becomes

$$Co = 58.826,$$

when $O = 15.96$.

In a second method metallic cobalt was dissolved in hydrochloric acid, and the solution evaporated to dryness with special precautions against dust. The chloride thus obtained was then dried at 150° in a stream of pure gaseous hydrochloric acid, so that basic salts could not be formed. From the weight of cobalt

[1] "Die Atomgewichts Bestimmung des Kobalts." A doctoral dissertation. Basel, 1895.

and of cobalt chloride the ratio $Co : Cl_2$ is determined. The chlorine was afterwards re-estimated as silver chloride, giving the ratio $Co : 2AgCl$. The weights are subjoined :

Co taken.	Cl taken up.	AgCl.
0.7010	0.8453	.....
0.3138	0.3793	.....
0.2949	0.3562	1.4349
0.4691	0.5657	2.2812
0.5818	0.7026	2.8303
0.5763	0.6947	.....
0.5096	0.6142	2.4813

Hence, with $Cl = 35.37$, and $Ag = 107.66$, $Co =$

$Co : Cl_2$.	$Co : 2AgCl$.
58.66	.....
58.52	.....
58.57	58.828
58.66	58.825
58.58	58.803
58.68	.....
58.69	58.750
Mean 58.64	Mean, 58.801

The second column is subject to a small correction for dissolved silver chloride, which reduces the mean to $Co = 58.770$. Reduced to a vacuum this becomes 58.765, and the value from the $Co : Cl_2$ ratio becomes 58.61. Thiele regards $Co = 58.765$ as the most probable value to be derived from his experiments. This becomes

With $O = 16$, $Co = 58.912$
" $O = 15.88$, $Co = 58.470$.

In my report for 1894 I gave Winkler's work on cobalt and nickel, which involved their ratios to iodine. In a supplementary paper Winkler[1] gives some similar experiments with iron, intended to show that errors due to metallic occlusion of hydrogen are absent from his determinations. He succeeds in proving that such errors, if they exist, must be very small. Thiele also considered their possibility, and guarded against them in the preparation of his cobalt.

Zinc.—Atomic weights redetermined by Richards and Rogers,[2]

1 *Ztschr. anorg Chem.*, 8, 291.

2 *Ztschr. anorg. Chem.*, 10, 1. Calculations made with $O = 16$, $Ag = 107.93$, and $Br = 79.955$.

who used the bromide method. Zinc bromide, carefully purified, was treated gravimetrically with standard silver solution. The weights and results are subjoined:

First, $ZnBr_2 : 2AgBr$.

$ZnBr_2$.	AgBr.	Atomic weight of Zn.
1.69616	2.82805	65.469
1.98198	3.30450	65.470
1.70920	2.84549	65.487
2.35079	3.91941	65.470
2.66078	4.43751	65.400
		Mean, 65.459

Second, same ratio.

$ZnBr_2$.	AgBr.	Atomic weight of Zn.
2.33882	3.90067	65.400
1.97142	3.28742	65.434
2.14985	3.58539	65.402
2.00966	3.35074	65.463
		Mean, 65.425

Third, $ZnBr_2 : Ag_2$.

$ZnBr_2$.	Ag.	Atomic weight of Zn.
2.33882	2.24063	65.409
1.97142	1.88837	65.444
2.14985	2.05971	65.396
2.00966	1.92476	65.472
		Mean, 65.430

Two additional series of data are given by Richards alone, as follows:

First, $ZnBr_2 : Ag_2$.

$ZnBr_2$	Ag.	Atomic weight of Zn.
6.23833	5.9766	65.403
5.26449	5.0436	65.404
9.36283	8.9702	65.392
		Mean, 65.402

Second, $ZnBr_2 : 2AgBr$.

$ZnBr_2$.	AgBr.	Atomic weight of Zn.
2.65847	4.43358	65.410
2.30939	3.85149	65.404
5.26449	8.77992	65.404
		Mean, 65.406

The final mean adopted by Richards is 65.404. With O = 15.88 this becomes

$$Zn = 64.913.$$

Cadmium.—Mr. Bucher's paper,[1] as its title indicates, is a study of methods rather than a final determination of atomic weight; but the results recorded in it compare well with those reached by others. His starting point is metallic cadmium, purified by nine distillations *in vacuo*, and from this material, with pure reagents, his various preparations were made. Vacuum weights are given, and the antecedent values used in calculation are O, 16; S, 32.059; C, 12.003; Cl, 35.45; Br, 79.95; and Ag, 107.93.

First, cadmium oxalate, dried for fifty hours at 150°, was decomposed by heat, and so reduced to oxide. The variations are mainly attributed to imperfect dehydration of the oxalate. Weights and results are as follows:

Oxalate.	Oxide.	Atomic weight of Cd.
1.97674	1.26474	111.74
1.94912	1.24682	111.83
1.97686	1.25886	111.85
1.87099	1.19675	111.81
1.37550	0.87994	111.86
1.33313	0.85308	111.96
1.94450	1.24452	112.02
2.01846	1.29210	112.09
	Mean,	111.89

Second, cadmium oxalate was transformed to sulphide by heating in a stream of hydrogen sulphide. The data are:

Oxalate.	Sulphide.	Atomic weight of Cd.
2.56319	1.84716	112.25
2.18364	1.57341	112.19
2.11643	1.52462	112.03
3.13105	2.25582	112.12
	Mean,	112.15

Third, cadmium chloride, dried at 300° in a stream of dry, gaseous hydrochloric acid, was precipitated by silver nitrate, and the silver chloride was collected with all necessary precautions. The weights and results are subjoined:

[1] "An examination of some methods employed in determining the atomic weight of cadmium." By John E. Bucher. Johns Hopkins University, doctoral dissertation. Baltimore (Friedenwald), 1895.

$CdCl_2$.	AgCl.	Atomic weight of Cd.
3.09183	4.83856	112.34
2.26100	3.53854	112.33
1.35729	2.12431	112.32
2.05582	3.21727	112.34
1.89774	2.97041	112.31
3.50367	5.48473	112.28
2.70292	4.23087	112.30
4.24276	6.63598	112.44
3.40200	5.32314	112.37
4.60659	7.20386	112.47
2.40832	3.76715	112.42
2.19144	3.42724	112.46
2.84628	4.45477	112.32
2.56748	4.01651	112.41
2.31003	3.61370	112.41
1.25008	1.95652	112.32
1.96015	3.06541	112.47
2.29787	3.59591	112.45
1.94227	3.03811	112.42
1.10976	1.73547	112.47
1.63080	2.55016	112.48
	Mean,	112.39

Fourth cadmium bromide was analyzed in much the same way as the chloride. The weights and results are as follows:

$CdBr_2$.	AgBr.	Atomic weight of Cd.
4.39941	6.07204	112.35
3.18030	4.38831	112.42
3.60336	4.97150	112.45
4.04240	5.58062	112.29
3.60505	4.97319	112.38
	Mean,	112.38

Fifth, cadmium sulphate was formed by synthesis from metallic cadmium. 1.15781 grams cadmium gave 2.14776 cadmium sulphate. Hence Cd = 112.35. As any impurity in the sulphate would tend to lower the atomic weight found, this is probably a minimum valve.

Sixth, metallic cadmium was converted into oxide by solution in nitric acid and ignition of the nitrate. The ignition was performed in double crucibles, both porcelain in experiments 1 and 2, the inner one of platinum in the rest of the series. Weights and results as follows:

Cd.	CdO.		Atomic weight of Cd.
1.26142	1.44144		112.12
0.99785	1.40135		112.04
		Mean,	112.08
1.11321	1.27247		111.84
1.02412	1.17054		111.91
2.80966	3.21152		111.87
		Mean,	111.87

In this case additional experiments were made to discover the sources of error, leading to corrections which bring the results near to those found in the chloride and bromide series. Each of the methods is quite fully discussed, and the sources of error are noted. With O = 16, 112.39 seems to be a close approximation to the true atomic weight of cadmium.

Molybdenum.—Seubert and Pollard,[1] by two distinct methods, have redetermined the atomic weight of this element. First, melybdenum trioxide was dissolved, in weighed quantities, in a standard solution of caustic soda. The excess of soda was then measured by titration with standard sulphuric acid and lime water. In another set of experiments the volumetric value of the caustic soda had been estimated with standard hydrochloric acid while the last compound had also been determined gravimetrically in terms of silver chloride. Hence the data, all considered together, give from their true end terms, the ratio $MoO_3 : 2AgCl$, although in a very indirect manner; and for this indirection the authors give good reasons. The weights and results, considering only the end terms, are as follows:

MoO_3.	AgCl.	Atomic weight of Mo.
3.6002	7.1709	95.734
3.5925	7.1569	95.708
3.7311	7.4304	95.757
3.8668	7.7011	95.749
3.9361	7.8407	95.720
3.8986	7.7649	95.740
3.9630	7.8941	95.723
3.9554	7.8806	95.694
3.9147	7.7999	95.686
3.8543	7.6767	95.740
3.9367	7.8437	95.688
	Mean,	95.722

[1] *Ztschr. anorg. Chem.*, 8, 434. Calculations on the basis of O = 15.96.

Reduced to vacuum standards this becomes Mo = 95.729. With O = 16, Mo = 95.969; and with O = 15.88, Mo = 95.249.

Another series of determinations, in confirmation of the first, was made by the old method of reducing molybdenum troxide in hydrogen. The weight and results are subjoined:

MoO_3.	Mo.	Atomic weight of Mo.
1.8033	1.2021	95.736
1.7345	1.1564	95.777
3.9413	2.6275	95.756
1.5241	1.0160	95.741
4.0533	2.7027	95.813
	Mean,	95.765

Reduced to vacuum, Mo = 95.735, a value very close to the other. When O = 16, the atomic weight of molybdenum is very near the even number 96.

Tellurium.—The determinations of atomic weight by Staudenmeier[1] all start our from telluric acid, $H_2TeO_4.2_2HO$, which had been purified by repeated crystallization. Two essentially different methods were adopted. First, telluric acid was dehydrated, and reduced to TeO_2 by heating. Secondly telluric acid was reduced by heating in hydrogen to metallic tellurium, finely divided silver being mixed with the acid to retain the tellurium by preventing volatilization. In four experiments, TeO_2 was reduced to Te in the same manner. The weights and results may be classified as follows, for convenience of comparison:

TeO_2 : Te.

TeO_2.	Loss on reduction.	Atomic weight of Te.
0.9171	0.1839	127.6
1.9721	0.3951	127.7
2.4115	0.4835	127.6
1.0172	0.2041	127.5

TELLURIC ACID; TeO_2.

Telluric acid.	Loss.	Atomic weight of Te.
1.7218	0.5260	127.2
2.8402	0.8676	127.1
4.0998	1.2528	127.1
3.0916	0.9450	127.05
1.1138	0.3405	127.0
4.9843	1.5236	127.05
4.6716	1.4278	127.1

[1] *Ztschr. anorg. Chem.*, 10, 189. Calculations based upon O = 16 and H = 1.0032.

TELLURIC ACID : TE.

Telluric acid.	Loss.	Atomic weight of Te.
1.2299	0.5471	127.3
1.0175	0.4526	127.3
2.5946	1.1549	127.2

There is a good discussion in the paper as to the possible causes of error in these determinations, and also concerning the place of tellurium in the periodic system. Staudenmeier upholds the homogeneity of tellurium as an element, as against the supposition that it is a mixture.

Some years ago Brauner, in an elaborate paper upon tellurium, sought to show that the ordinary element was a mixture of true tellurium with a higher homologue of atomic weight 214. He now[1] concludes that this is very improbable, and suggests that tellurium may contain a homologue of argon, of atomic weight 130. For this supposition no evidence is given apart from the abnormality of the atomic weight, which should fall below that of iodine.

Yttrium.—The atomic weight of this metal has been redetermined by Jones,[2] who starts out with material purified by Rowland's process, that is, by precipitation with potassium ferrocyanide. First, oxide was converted into sulphate ; and secondly, sulphate was transformed to oxide by calcination. The weights and results were as follows :

FIRST METHOD.

Y_2O_3.	$Y_2(SO_4)_3$.	Atomic weight of Y.
0.2415	0.4984	88.89
0.4112	0.8485	88.92
0.2238	0.4617	88.97
0.3334	0.6879	88.94
0.3408	0.7033	88.90
0.3418	0.7049	89.05
0.2810	0.5798	88.94
0.3718	0.7803	88.89
0.4379	0.9032	89.02
0.4798	0.9901	88.91
	Mean,	88.94

[1] *J. Chem. Soc.*, 67, 549.

[2] *Am. Chem. J.*, 17, 154. Calculations made with O = 16, and S = 32.06.

SECOND METHOD.

$Y_2(SO_4)_3$.	Y_2O_3.	Atomic weight of Y.
0.5906	0.2862	88.91
0.4918	0.2383	88.89
0.5579	0.2705	89.03
0.6430	0.3117	88.99
0.6953	0.3369	88.89
1.4192	0.6880	88.99
0.8307	0.4027	88.99
0.7980	0.3869	89.02
0.8538	0.4139	88.99
1.1890	0.5763	88.96
	Mean,	88.97

These determinations are probably the best hitherto made, although they have been briefly criticized by Delafontaine,[1] who prefers the lower value obtained by himself, Y = 87.3. Delafontaine reaffirms the existence of phillipium, and regards gadolinium as identical with decipium. Jones,[2] in a brief rejoinder, defends his own work, and urges that Delafontaine has failed to show wherein it is defective.

The Cerite Earths.—Papers upon this subject have been published during the year by Schutzenberger and by Brauner. In his first communication, Schutzenberger[3] deals with cerium, which had been freed from lanthanum and "didymium" by fusion of the mixed nitrates with saltpeter. The yellowish-white cerium oxide was converted into cerium suiphate, which was dried at 440°. In this salt, with special precautions, the sulphuric acid was estimated by precipitation with barium chloride. One hundred parts of cerium sulphate gave 123.30 of barium sulphate. Hence, Ce = 139.45, according to Schutzenberger's calculations. Recomputing, with

$$O = 16,\ S = 32.07,\ \text{and}\ Ba = 137.43,$$
$$Ce = 139.96.$$

In a second paper,[4] Schutzenberger describes the results obtained by the fractionation of cerium sulphate. Preparations were thus secured giving oxides of various colors, such as canary yellow, yellowish rose, reddish, and brownish red. These,

[1] *Chem. News*, 71, 243.
[2] *Chem. News*, 71, 305.
[3] *Compt. rend.*, 120, 663.
[4] *Compt. rend.*, 120, 962.

by the synthesis of the sulphates, the barium sulphate method, etc., gave varying values for cerium ranging from 135.7 up to 143.3. Schutzenberger concludes that the cerium sesquioxide from cerite contains small quantities of another earth of lower atomic weight. In a third paper[1] he continues the investigation with the other cerite earths. For the didymiums he finds a range in atomic weight from 137.5 to 143.5, approximately.

Brauner's paper[2] is partly a reclamation of priority over Schutzenberger, and partly a preliminary statement of new results. In his earlier work he found that cerium oxide was a mixture of two earths; one white, the other flesh color with a tinge of orange, and atomic weights for the contained metal of 140.2 and 145.72, respectively. In his later research Brauner fractionates his material by several methods. One constituent obtained from cerium oxide is a dark salmon-colored earth, the oxide of a metal which he calls "meta-cerium." The other constituent he calls cerium. Pure cerium oxalate by Gibbs' permanganate method gave 29.506 and 29.503 per cent. of cerium sesquioxide with 46.934 per cent. of cerium dioxide. Hence, Ce = 139.91, or, with a slight correction, Ce = 140.01. This is not far from Schutzenberger's value.

Helium and Argon.—The true atomic weights of these remarkable gases are still in doubt, and so far can only be inferred from their specific gravities. For argon, the discoverers, Rayleigh and Ramsay,[3] give various determinations of density, ranging (H = 1) from 19.48 to 20.6. The value 19.9 they regard as approximately correct.

For helium, Ramsay[4] gives the density 2.18, while Langlet[5] finds the somewhat lower value 2.00.

From one set of physical data, both gases appear to be monatomic, but from other considerations they are supposably diatomic. Upon this question, controversy has been most active, and no final settlement has yet been reached. If diatomic, argon and helium have approximately the atomic weights, two

1 *Compt. rend.*, 120, 1143.
2 *Chem. News*, 71, 283.
3 *Phil. Trans.*, 186, 220–223.
4 *J. Chem. Soc.*, 3, 684.
5 *Ztschr. anorg. Chem.*, 10, 289.

and twenty, respectively; if monatomic, these values must be doubled. In either case, helium is an element lying between hydrogen and lithium; but argon is most difficult to classify. With the atomic weight 20, argon fills in the eighth column of the periodic system, between fluorine and sodium; but if it is 40, the position of the gas is anomalous. A slightly lower value would place it between chlorine and potassium, and again in the eighth column of Mendejeff's table, but for the number 40 no opening can be found.

It must be noted that neither gas, so far, has been proved to be absolutely homogeneous; and it is quite possible that both may contain admixtures of other things. This consideration has been repeatedly urged by various writers. If argon is monatomic, a small impurity of greater density, say of an unknown element falling between bromine and rubidium, would account for the abnormality of its atomic weight, and tend towards the reduction of the latter. If the element is diatomic, its classification is easy enough on the basis of existing data. Its resemblances to nitrogen, as regards density, boiling point, difficulty of liquefaction, etc., lead me personally to favor the lower figure for its atomic weight, and the same considerations may apply to helium also. Until further evidence is furnished, therefore, I shall assume the values two and twenty as approximately true for the atomic weights of helium and argon.

Carbon.—Wanklyn,[1] on the basis of his investigations into the composition of hydrocarbons, reiterates his belief that the atomic weight of carbon is not 12, but 6. This question is one which falls rather outside the scope of this report and needs no further discussion here. If Wanklyn's contention is sustained, the value assigned to carbon in the table at the close of this paper, should be divided by two.

In the following table of atomic weights, the values are given according to both standards, H = 1 and O = 16. Many of the figures are the results of new and complete recalculations from all available data, made in the preparation of a new edition of my "Recalculation of the Atomic Weights." This work is now well under way, and it will probably be completed during 1896:

[1] *Chem. News.* 72, 164. See also *Phil. Mag.*, August, 1895. Also the reports of this committee for 1893 and 1894.

	H = 1.	O = 16.
Aluminum	26.91	27.11
Antimony	119.52	120.43
Argon	?	?
Arsenic	74.52	75.09
Barium	136.40	137.43
Bismuth	206.54	208.11
Boron	10.86	10.95
Bromine	79.34	79.95
Cadmium	111.08	111.93
Cesium	131.89	132.89
Calcium	39.78	40.08
Carbon	11.92	12.01
Cerium	139.1	140.2
Chlorine	35.18	35.45
Chromium	51.74	52.14
Cobalt	58.49	58.93
Columbian	93.3	94.0
Copper	63.12	63.60
Erbium	165.0	166.3
Fluorine	18.89	19.03
Gadolinium	154.9	156.1
Gallium	68.5	69.0
Germanium	71.75	72.3
Glucinum	9.01	9.08
Gold	195.74	197.24
Helium	?	?
Hydrogen	1.00	1.008
Indium	112.8	113.7
Iodine	125.89	126.85
Iridium	191.66	193.12
Iron	55.60	56.02
Lanthanum	137.6	138.6
Lead	205.36	206.92
Lithium	6.97	7.03
Magnesium	24.11	24.29
Manganese	54.57	54.99
Mercury	198.5	200.0
Molybdenum	95.26	95.98
Neodymium	139.4	140.5
Nickel	58.24	58.69
Nitrogen	13.94	14.04
Osmium	189.55	190.99
Oxygen	15.879	16.00
Palladium	105.56	106.36
Phosphorus	30.79	31.02

Platinum	193.41	194.89
Potassium	38.82	39.11
Praseodymium	142.4	143.5
Rhodium	102.23	103.01
Rubidium	84.78	85.43
Ruthenium	100.91	101.68
Samarium	148.9	150.0
Scandium	43.7	44.0
Selenium	78.4	79.0
Silicon	28.18	28.40
Silver	107.11	107.92
Sodium	22.88	23.05
Strontium	86.95	87.61
Sulphur	31.83	32.07
Tantalum	181.2	182.6
Tellurium	126.1?	127.0?
Terbium	158.8	160.0
Thallium	202.60	204.15
Thorium	230.87	232.63
Thulium	169.4	170.7
Tin	118.15	119.05
Titanium	47.79	48.15
Tungsten	183.44	184.84
Uranium	237.77	239.59
Vanadium	50.99	51.38
Ytterbium	171.7	173.0
Yttrium	88.28	88.95
Zinc	64.91	65.41
Zirconium	89.9	90.6

COMPOSITION OF WOOD GUM.

By S. W. JOHNSON.

Received January 20, 1896

SINCE 1879, when Thomsen published his investigation of "Wood Gum," the writer has, from time to time, as opportunity offered, employed several of the chemists of the Connecticut Agricultural Experiment Station in work upon the alkali-soluble carbohydrates of maize cobs, birch wood and vegetable ivory. This work has necessarily been subject to frequent and prolonged interruptions, and for that reason the publication of conclusive results has been greatly delayed.

Wood gum, which is abundantly extracted from the wood of deciduous trees by cold, weak (two to ten per cent.) solutions of

sodium or potassium hydroxide, and thrown down therefrom by neutralization and by alcohol, has been analyzed by Thomsen, Koch, Schuppe and by Wheeler and Tollens.[1]

With exception of Schuppe, all these investigators obtained results on the whole agreeing fairly with the formula $C_5H_{10}O_5$.

Schuppe's analyses mostly gave higher figures for carbon and hydrogen.

Xylan.—When it was shown by Wheeler and Tollens that xylose, the sugar first described by Koch, and obtained by him, from the products of the hydrolysis of wood gum, has the formula $C_5H_{10}O_5$, it became extremely probable that the corresponding anhydride, now designated xylan, has the composition $C_5H_8O_4$.

Analyses made in this laboratory in 1885 demonstrated that the cobs of Indian corn yield to five or ten per cent. potassium hydroxide solution, a body, which, precipitated by alcohol, acidulated with hydrochloric acid, suitably washed and thoroughly dried, has in fact the composition proper to pure xylan.

In 1880 xylan was thus prepared under my direction by Dr. Jenkins, as follows: Ground maize cob was digested for twenty-four hours with frequent agitation in a mixture of one volume of concentrated ammonia with seven volumes of water, the residue was washed on filters to remove all ammonia and digested forty-eight hours with seven per cent. caustic soda solution. The filtered extract was mixed with twice its volume of ninety-three per cent. alcohol. The precipitate was washed until the washings were neutral to test papers, then was stirred up with dilute hydrochloric acid, again washed with dilute alcohol until neutral and thereupon was further treated with absolute alcohol and ether and dried over sulphuric acid. About twenty-five per cent. of white, easily powdered material were thus obtained, which answered to Thomsen's description of wood gum.

It was not made blue by iodine solution. Agitated with pure water at common temperatures for a considerable time, it was taken up to the extent of 0.14 per cent., giving a neutral solution. Boiled for six hours with water, a neutral solution resulted, which contained 0.44 per cent. of dissolved substance that very slightly reduced Fehling's solution. The solution in hot water was unaf-

[1] *Ann. Chem.* (Liebig), **254**, 320.

fected by addition of normal lead acetate, but with basic lead acetate gave a heavy flocculent precipitate. Our earlier analyses of this substance gave varying results, due, it may be, partly to impurities, but doubtless largely attributable to its avidity for moisture and the difficulty of drying it completely or of holding it at a constant moisture content.

We could obtain no accordant analyses except by weighing off in quick succession several portions of the air-dry substance that had been fully exposed to air and was neither gaining nor losing moisture, determining carbon and hydrogen in some of these portions and moisture in others, with such precautions as to preclude change of water content.

Hygroscopic water we determined most satisfactorily by drying *in vacuo* at 110°–112°C. For this purpose the substance was contained in a stout glass tube about three cm. wide and ten cm. long, sealed off round at the base and narrowed above to a neck two cm. wide. This was connected by a perforated cork with a water pump, giving a vacuum equal to twenty-eight to twenty-nine and one-half cm. of mercury column, and was heated by placing within a close fitting vertical well, whose sides and bottom were surrounded by boiling aqueous solution of sodium nitrate contained in a closed copper box, the vapor from which was constantly returned by means of an efficient condenser. The glass drying tube, well corked, was counterpoised on the balance by a similar corked tube, and suitable precautions were used to avoid or compensate any changes of moisture of glass or corks.

Recurring to the already published statements, we note that the chemists whose analyses gave results mostly agreeing fairly with the formula $C_6H_{10}O_5$ are silent (in the accounts I have been able to refer to) as to their mode of drying, so Thomsen and Koch, or as in case of Wheeler and Tollens, analyzed "substance that had been dried over sulphuric acid and warmed for some hours at 97° in a water oven."

Mr. Winton, in this laboratory, found that two samples of finely subdivided air-dry wood gum from maize cobs required six days exposure to concentrated aud recently boiled oil of vitriol to come to constant weight, with loss of 8.10 per cent. and

8.11 per cent. and thus dried further lost in three and one-half hours at 100° in a current of dried hydrogen in one case 0.67 per cent., and in another 1.83 per cent., and on further heating in hydrogen for two hours at 120°, lost 0.07 and 0.25 per cent. respectively.

But while it may not be difficult to bring wood gum nearly to complete dryness in the water oven, it is not easy to weigh off, transfer to a combustion tube and burn this dried substance without its taking up sufficient moisture to vitiate an analysis, especially when the atmosphere is humid.

In 1880, Dr. Jenkins, following the methods then in use in this laboratory, made his first analyses of air-dry xylan, determining water by prolonged drying in a water oven. In three combustions he obtained, reckoned on dry matter, 45.25, 45.48 and 45.72 per cent. of carbon respectively. His hydrogen determinations, however, were more irregular, *viz.* : 6.37, 7.35 and 5.90 per cent.

Dr. Jenkins next imperfectly dried his stock of xylan at 100° and weighed off the portions for analysis as required. In four combustions, reckoned ash free, carbon ranged from 44.34 to 45.20 per cent., and hydrogen from 5.92 to 6.01. His averages were: carbon, 44.81 ; hydrogen, 5.96. These results are quite like those from which Thomsen, Koch, and Wheeler and Tollens deduced the formula $C_5H_{10}O_5$.

Subsequently in 1883, Mr. (now Professor) Milton Whitney, devoted considerable time to analyses of various preparation of wood gum, sometimes using air-dry material, at others substance dried at 100°, but without reaching altogether satisfactory results.

Finally, after I, with Mr. Winton's aid, had accurately ascertained the conditions for completely desiccating this substance and the precautions needful in handling it, it became easy to fix its composition.

In 1885 Dr. Osborne made analyses of a sample of wood gum prepared by Mr. Whitney from corn cobs, being a first fraction thrown down by adding about one-half the amount of alcohol needful for complete precipitation of the soda-lye extract, and otherwise treated as before described. About two grams of this xylan required in one case near six hours heating at 112° in a

vacuum maintained at 29.0 to 29.5 inches mercury, and in another case when the vacuum ranged from 28.5 to 28.0 inches, needed nine hours heating at 112° for reaching constant weights. In either case the loss was 13.51 per cent., and further heating for three hours occassioned no change either in the weight or color of the substance.

Dr. Osborne's combustions of air-dry substance furnished results as follows :

	I.	II.	III.	Average.
Carbon	39.12	39.10	39.06	39.09
Hydrogen	6.81	6.65	6.73	6.73
Ash	0.59	0.66	0.59	0.61
Moisture	....	....	....	13.51

The above average reckoned on dry and ash-free substance is :

		Calculated for $C_6H_8O_4$.
Carbon	45.51	45.45
Hydrogen	6.09	6.16
Oxygen	48.40	48.49
	100.00	100.00

In another similar preparation Dr. Jenkins demonstrated the absence of nitrogen by soda lime combustion.

In two other preparations the ash contents were found to be respectively 0.23 and 1.73 per cent.

At my request Mr. E. B. Hurlburt has lately hydrolyzed corn cob xylan prepared in 1880 and obtained a syrup which, after seeding with a little pure xylose,[1] in a few days, nearly solidified to a mass of crystals that when washed with alcohol and dried, melted at 153° C.

It thus appears that the cobs of Indian corn yield very pure xylan, $C_6H_8O_4$.

It is also probable that many of the analyses of wood gum hitherto published, those of Schuppe possibly excepted, were made on imperfectly dried material, and for that reason mainly, gave results leading to the incorrect formula $C_6H_{10}O_5$.

Birch Wood Gum.—Preparations obtained from the wood of the American white, or gray birch, *Betula alba*, differ in compo-

[1] Kindly supplied for this purpose by Prof. W. E. Stone, who was the first to announce the preparation of xylose from maize cobs.

sition from the xylan of maize cob. Dr. Osborne found in the air-dry substance of one sample:

	I.	II.	Average.
Carbon	42.69	42.49	42.59
Hydrogen	6.65	6.59	6.62
Ash	0.65	0.64	0.65
Moisture	....	....	9.84

Moisture was determined by drying *in vacuo* at 112° C. Constant weight was obtained in one determination in six hours with 29.5 inches of mercury in manometer, the loss being 10.26 per cent., and in another in twelve hours with twenty-eight inches of mercury, the loss being 9.42 per cent.

The average results reckoned on substance free from moisture and ash are:

		Calculated for $C_4H_6O_3$.
Carbon	47.58	47.06
Hydrogen	6.17	5.88
Oxygen	46.25	47.06

These figures for carbon are two per cent. higher than those belonging to the pentosans, and come nearer the composition of a tetrosan.

The birch wood gum, when hydrolyzed, yields a syrup from which, on long standing, or by fractioning with alcohol, a very small proportion of crystals may be separated, which do not appear to be increased in quantity by "seeding" with crystallized xylose.

The further study of birch wood gum and the products of its hydrolysis is reserved.

Mannan.—When the sugar obtained by Reiss[1] from vegetable ivory, the fruit of *Phytelephas*, as the results of hydrolysis, was shown by E. Fischer to be mannose, it became evident that the substance yielding this sugar is a carbohydrate of composition corresponding to the formula $C_6H_{10}O_5$.

According to Reiss,[2] vegetable ivory yields near seven and five-tenths per cent. of a water-soluble carbohydrate, which in the dry state is a yellowish brown gummy mass, having left-handed polarization, readily hydrolyzed and then yielding the

[1] *Ber. d. Chem. Ges.*, 22, 609.

[2] Landwirthschaftliche Jahrbücher, 18, 745, *1889*.

sugar mannose. The vegetable ivory also contains or yields, according to Reiss, a carbohydrate in large proportion, which he prepared as a white amorphous powder by digesting vegetable ivory shavings with an equal weight of seventy per cent. sulphuric acid for twenty-four hours, then adding to the mixture its weight of water, filtering, adding a little alcohol to throw down impurities, and lastly precipitating with mixed alcohol and ether, washing and drying the product. This substance, which Reiss found to swell and partially dissolve in water, and to be laevorotatory and to reduce Fehling's solution, was termed by him seminin and by Tollens[1] paramannan. It yielded mannose on hydrolysis, but its composition, so far as I am aware, has not been determined.

Several investigators have inferred the existence of mannan in seeds of coffee, date, nux vomica, *Diospyros*, cocoanut, and pine wood, etc., from the formation of an insoluble hydrazone in the products of the hydrolysis of these materials, but only Reiss, I believe, has attempted to separate the carbohydrate from the associated substances.

In the year 1880 a quantity of refuse vegetable ivory was sent to this station for examination, with the statement that "it had been used as feed for cattle, which ate it with great relish and fattened upon it."[2]

A "fodder analysis" was accordingly made, the results of which were as follows:

Water (at 100° C.)	18.78
Ash	1.08
Crude fat (ether extract)	0.70
Albuminoids (N × 6.25)	3.37
Crude fiber	7.50
Nitrogen-free extract (by difference)	68.57
	100.00

It was at the same time found that vegetable ivory yields to

[1] Ladenburg's Handwörterbuch, **13**, 755.

[2] Loew and Ishii have recently stated that the root of *Conophallus konnjaku*, which is used as human food in Japan, contains mannan, *i. e.*, yields mannosehydrazone in considerable quantity. (Versuchsstationen, **45**, 435.) Salep mucilage, formerly used as food for invalids, also very probably contains mannan or a mannocellulose. (Gans and Tollens: *Ann. Chem.*, (Liebig), **249**, 256.)

soda lye a large proportion of substance resembling "wood gum," and a number of preparations were made in 1880 by Dr. Armsby, and in 1883 by Mr. (now Professor) Milton Whitney.

Mr. Whitney also analyzed six of these preparations. His mode of drying was long exposure to concentrated sulphuric acid and subsequent heating for one hour in the water oven.

The results of these analyses were not altogether uniform, but either by excluding extremes or taking the average they fairly agreed with the formula $4(C_6H_{10}O_5)\ H_2O$, which requires two and seven-tenths per cent. of hydrate water. This water, however, was doubtless merely hygroscopic.

After having ascertained the precise conditions for determining moisture in various specimens of wood gum, I requested Dr. Osborne in 1885 to analyze two of Dr. Armsby's vegetable ivory preparations then remaining. To determine moisture the air-dry material was heated *in vacuo* (28.0 to 29.5 inches of mercury) at 112° C. for eight to nine hours to constant weight. In one case the substance was further heated for three hours without change in weight or appearance.

The combustions were made on portions of the same air-dry substance as served for estimating moisture.

The following are Dr. Osborne's results:

SAMPLE B. I. 2, AIR-DRY.

	I.	II.	III.	IV.	Average.
Carbon	....	....	40.08	40.17	40.13
Hydrogen	....	....	6.82	6.82	6.82
Ash	....	....	0.10	0.16	0.13
Moisture	9.59	9.65	....	....	9.62

SAMPLE B. II. 1, AIR-DRY.

	I.	II.	III.	IV.	Average.
Carbon	....	....	39.14	39.19	39.17
Hydrogen	....	....	6.92	6.90	6.91
Ash	....	....	trace	trace	trace
Moisture	10.88	10.88	....	....	10.88

The dry ash-free mannan has accordingly the subjoined composition:

	B. I. 2.	B. II. 1.	Calculated for $C_6H_{10}O_5$.
Carbon	44.46	43.95	44.44
Hydrogen	6.37	6.39	6.17
Oxygen	49.17	49.66	49.38
	100.00	100.00	100.00

The mannan of vegetable ivory may be separated in fractions by adding alcohol to its solution in sodium hydroxide.

Armsby's preparation B. I. 2 and B. II. 1 were obtained as follows: One kilo of vegetable ivory turnings was digested for twenty-four hours in a mixture of 800 cc. concentrated ammonia and five and a half liters of water and washed with water until ammonia was removed. The residue was digested twenty-four hours in a solution of 800 grams potassium hydroxide in eight liters of water and filtered, giving a first extract B. I. The undissolved substance was then treated for twenty-four hours with a solution of 480 grams potassium hydroxide in six liters of water and filtered. The second extract was marked B. II.

The potash extract B. I. was mixed with about three-sixteenths of its bulb of ninety-three per cent. alcohol, and allowed to stand an hour; the turbid liquid was separated from the precipitate by decantation and filtration. This first precipitate was B. I. 1. The filtrate therefrom was completely precipitated by its own volume of alcohol, and the second precipitate was B. I. 2, whose analyses correspond so closely to $C_6H_{10}O_5$.

The soda extract B. II. with rather more than one-fourth its bulk of alcohol gave B. II. 1, (containing five-tenths per cent. less carbon than B. I. 2.), and the filtrate therefrom with excess of alcohol yielded a second small precipitate B. II. 2.

These precipitations, after removing mother liquors, were washed with sixty-six per cent. alcohol until nearly neutral, then digested with excess of dilute hydrochloric acid for a day and finally washed out completely with sixty-six per cent., eighty per cent., and absolute alcohol and with ether in succession.

It thus appears that vegetable ivory may yield to dilute caustic alkali solutions a nearly or entirely pure mannan, and that this body is probably accompanied with an alkali-soluble substance of lower carbon content.

METHOD FOR THE DETERMINATION OF CARBON IN STEEL.

By Andrew A. Blair.

Received January 14, 1896.

THE method given below for the determination of carbon in steel is generally used in the steel works laboratories in the Eastern part of France, and I am indebted for the details to Monsieur H. A. Brustlein of the Aciéries d'Unieux at whose words and at those of the Aciéries de la Marine at Saint Chamond the various improvements in the method have been worked out.

The method was first suggested by Wiborg[1], but was very imperfect in its original form. The greatest improvement was suggested by Monsieur de Nolly of the Laboratory of the Aciéries de la Marine at Saint Chamond and consists in the addition of phosphoric acid to the oxidizing mixture by which the iron is much more rapidly dissolved and the use of a considerable amount of chromic acid is rendered possible without the evolution of a large volume of oxygen gas.

The solutions employed are:

1. A saturated solution of chemically pure cupric sulphate.

2. An aqueous solution of chromic acid (one gram chromic acid to one cc. water).

3. A mixture of sulphuric, phosphoric and chromic acid made up as follows:

Solution of chromic acid (Sol. No. 2)	35 cc.
Water	115 "
Concentrated sulphuric acid	750 "
Phosphoric acid 1.4 sp. gr.	315 "

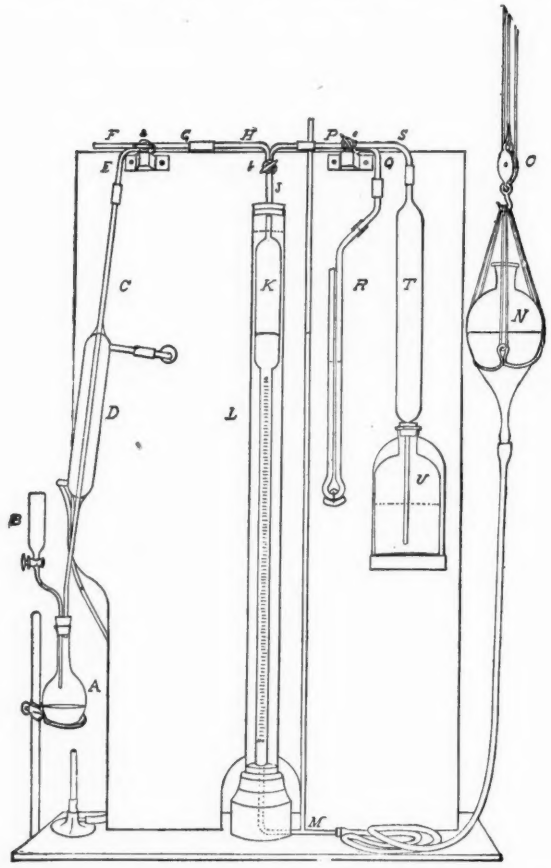
In preparing solution No. 2, add a few cc. of sulphuric acid and heat to boiling to destroy any organic matter that may be present.

In preparing solution No. 3, heat it to boiling also for the same purpose.

The apparatus as shown in the sketch consists of a round bottom Flask *A* of 200 cc. capacity with a long neck. The flask is closed with a rubber stopper with two holes, in one of

[1] Stahl und Eisen, 1882.

which is fitted the glass stopper funnel *B* and in the other the tube *C* enclosed in the condenser *D* through which a stream of water runs during the operation. The tube *C* is connected with



one tube *E* of a three way stop-cock *a*, from which the second tube *F* opens into the air and the third *G* connects with the tube *H* of the three way stop-cock *b*. The second tube *J* from

this stopcock is fused to the burette *K* which is enclosed in the tube *L* containing water. The lower end of the burette connects with a capillary tube *M* which serves as a level tube and is in the form of a T; it is connected with the mercury reservoir *N* which is raised and lowered by the arrangement *O*. The third tube of the stopcock *b* connects with the tube *P* of the stopcock *c*, the second tube *Q* of the stopcock *c* connects with the manometer *R* and the third tube *S* with the pipette *T* which runs into the bottle *U*. The tubes of the stopcocks *b* and *c*, the manometer tube *R*, the level tube *M* and the tubes of the pipette *T* are capillaries. The manometer tube *R* contains water and serves to accurately adjust the levels when taking the reading of the burette *K*. When the manometer is shut off from the burette the approximate level is ascertained by means of the level tube *M*. The tube *F* of the stopcock *a* is used only in exceptional cases: First, when the evolution of gas is insufficient to carry the mercury far enough down the burette *K*, in which case air is drawn through it into the burette; and secondly, when the evolution of gas is so great that it is necessary to make two asborptions in the pipette *T*, in which case the residue from the first absorption is discharged through the tube *F*. The pipette *T* contains a solution of potassium hydroxide of 1.27 sp. gr., and is of about 400 cc. capacity. The bottle *U* is of about one liter capacity. The water in the containing tube *L* serves to keep the gas in the burette at the ordinary temperature of the laboratory. It should be protected from the heat of the burner and flask by a screen.

The operation is conducted as follows:

Connect the pipette *T* by means of the stopcocks *b* and *c* with the burette *K* and, by lowering the mercury reservoir, fill the pipette with the potassium hydroxide solution, close the stopcock *c*, fill the burette *K* with mercury and close the stopcock *b*. Weigh one gram of drillings into the flask *A*, attach it to the apparatus, start the water through the condenser *D*, and connect the flask with the burette *K* by means of the stopcock *a*. Pour fifteen cc. of the cupric sulphate solution No. 1 into the funnel tube *B*, and let it flow into the flask. Allow it to act long enough to form a superficial deposit of copper on the

drillings (one or two minutes is sufficient) then add, through the funnel tube, fifteen cc. of solution No. 2 and 135 cc. of solution No. 3. Heat the solution in the flask and raise it slowly to the boiling point. By means of the reservoir, keep the mercury in the burette and in the tube *M* nearly level. The water condensed in the tube *C* drops back into the flask and keeps the liquid of the same density, while the properly cooled gases pass into the burette.

Allow the flask *A* to cool for about five minutes and then run into it, through the funnel tube *B*, enough water to fill the flask and the tube to the stopcock *a*, thus forcing all the gas into the burette. Close the stopcock *a* and connect the burette by means of the stopcocks *b* and *c* with the manometer *R*, adjust the levels accurately and take the reading of the burette. Then by means of the stopcock *c* connect the burette with the pipette *T* and by raising and lowering the reservoir *N*, pass the gas several times back and fourth to cause the potassium hydroxide to absorb all the carbon dioxide. Finally connect the burette with the manometer tube *R*, adjust the levels and take the reading of the burette.

The burette *K* should contain a few drops of water to insure the saturation of the gases with aqueous vapor. The difference between the two readings is the volume of the carbon dioxide. Observe the readings of the thermometer and barometer and reduce the volume of the carbon dioxide to that which it would occupy in the dry state at 0°C. and 760 mm. pressure.

Multiply the volume of the gas so obtained by 0.0019663 and the result is the weight of the carbon dioxide in grams.

I have constructed the apparatus as here described, and am satisfied that the results obtained by its use when the details of the method are carefully carried out are much more accurate than those arrived at by any other than the combustion method. Blank determinations at Unieux rarely give more than one-tenth cc. or two-tenths cc., when the solutions are properly purified. As results may be obtained in an hour and a half, the method should recommend itself to the chemists of steel works where determinations of carbon are called for in treated and special steels where the color method is inadmissable.

It may be noted here that the use of a condenser and the solutions given above will add to the accuracy of the method in which the carbon dioxide is weighed instead of measured.

LABORATORY OF BOOTH, GARRETT & BLAIR,
PHILADELPHIA.

A NEW SAFELY DISTILLATION TUBE FOR RAPID WORK IN NITROGEN DETERMINATIONS.

BY CYRIL G. HOPKINS.
Received December 12, 1895.

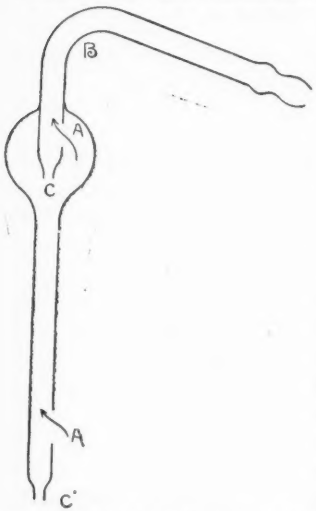
IN doing a large amount of work with fodders and fertilizers, involving several hundred determinations of nitrogen (by the Kjeldahl method), I have observed that the distillation tube (generally known as "Kjeldahl's connecting bulb tube," but doubtless more properly as Reitmeir's distillation tube) is frequently a source of error, due to the fact that it allows fixed alkali to be carried over mechanically. Especially in this the case when the distillation is carried on rapidly, and also when the contents of the distillation flask has a tendency to "bump."

In doing rapid work I have always found it necessary to have the lower end of these tubes reground before they would allow the liquid condensed in the bulb to run back into the distillation flask. Even after this is properly done the lower end of the tube is still open, and when the liquid boils violently or "bumps," small particles of it are often thrown up through the tube into the bulb. Sometimes these particles of strongly alkaline liquid strike the curved tube within the bulb, flow out to the end, and are forced into the tube and over into the condenser by the rapid current of vapor. This action is easily observed when the contents of the distillation flask is highly colored; and I find that the occurrence is familiar to chemists who have had much to do with nitrogen determinations.

I have obtained good results, however, by having the end of the tube within the distillation flask properly ground, and then protected by a larger glass tube, fastened to the distillation tube just below the rubber stopper, by means of a short piece of rubber tubing, and having an opening on the side and a jet at the lower end. This modification gave such good satisfaction that it finally led me to make a new distillation tube in which

not only the tube which passes into the distillation flask, but also the tube within the bulb has an opening on the side and a jet at the end.

The form of this distillation tube and its advantages over the tube in ordinary use will be plainly seen in the accompanying illustration.



The vapor passes in through the side openings A and A', and whatever condenses in the tube below the point B passes back into the distillation flask through the jets C and C'.

The possibility of liquid from the distillation flask being thrown into the tube is avoided, and the current of vapor does not interfere with the return of condensed liquid. The jets C and C' are two mm. inside diameter and they always remain filled with returning liquid when in use. The tubing used in making these distillation tubes is from seven mm. to eight mm. inside diameter. The side openings A and A' should be nearly as large, and the bulb, about five cm. in diameter. The length of the tube below the bulb is twelve cm. and that above the bulb about the same.

UNIVERSITY OF ILLINOIS, EXPERIMENT STATION.

REMARKS ON MR. AUCHY'S PAPER ON THE VOLUMETRIC DETERMINATION OF MANGANESE.

BY GEORGE C. STONE.

Received January 11, 1896.

IN the December number of the Journal of the American Chemical Society there is a paper by Mr. George Auchy on the "Volumetric Determination of Manganese," in which he advocates the use of Volhard's method, in which I heartily agree

[1] Read before the New York Section.

with him, but the method as he describes it, seems to me unnecesarily complicated.

Mr. Auchy criticises Williams' method and refers to the discussion of it which occurrred some years since.[1] At that time I satisfied myself that the method as originally described by Williams was not accurate, but in a modified form I used it for several years with good results until I, too, was treated to the same disagreeable surprise as Mr. Auchy, a member of manganese determinations came very low. On examination I found that this was due to the decomposition of the oxalic acid solution. I then gave up the method and have since used Volhard's with uniformly satisfactory results, except where there are only a few hundredths of a per cent. of manganese present, in which case I found the method of oxidizing by peroxide of lead, reducing by standard arsenious acid and titrating back by permanganate to work well.

Volhard's method, as I have used it, is as follows: The quantity of material taken for analysis should contain between 0.05 and 0.15 grams of manganese. If it is an alloy, dissolve in nitric acid of about 1.10 sp. gr.; if an ore or cinder, dissolve in hydrochloric acid and boil with a little potassium chlorate. In either case use but a small excess of acid. Cool, wash into a half liter flask with cold water and add an emulsion of zinc oxide until the precipitate curdles; the change in the appearance of the precipitate is sharp and distinct. Dilute to the mark, mix thoroughly, pour into a beaker and allow the precipitate to settle. Decant off exactly 100 cc. into a four inch casserole, dilute to about 200 cc., heat nearly to boiling and titrate rapidly with permanganate, one cc. of which should equal 0.001 gram of manganese (about 1.99 grams potassium permanganate in one liter). The greater part of the permanganate should be added at once and the solution very vigorously stirred. For this purpose a glass rod bent to a hook is very convenient, the hook of course being in the solution.

I have made a number of experiments to see if it makes any difference whether nitric, hydrochloric or sulphuric acid is used, and have not found that it does, provided the iron is oxidized. For

[1] Trans. Am. Inst. Min. Eng., 11, 514; 12, 295-449; *Chem. News*, 1883, 176-273.

neutralizing I use commercial zinc oxide, which contains a trifling amount of manganese, but under the conditions in which it is used this apparently does not go into solution. To test this point, I made a number of duplicate analyses, neutralizing one of each pair with zinc oxide and the other with barium carbonate; in all cases the results agreed well. It is not necessary to filter the solution; the iron precipitate settles very rapidly and completely, and if a little of the precipitate goes with the solution, it makes no difference. I think the trouble Mr. Auchy mentions in getting good results with steels low in manganese when a large excess of zinc oxide is used, is due to not having sufficient manganese present, as it is difficult to make a very small precipitate clot together so as to give a clear solution in which the color of the end reaction shows distinctly. I have often tried adding a very large excess of zinc oxide, but have never found it to interfere, provided the manganese was within the limits given above.

The method is very rapid, a determination of manganese in spiegel can easily be made in half an hour; ores usually take a little longer, as they are more difficult to dissolve.

PROBABLE PRODUCTION OF PERMANGANATE BY DIRECT COMBUSTION OF METALLIC MANGANESE.[1]

By George C. Stone.

Received January 11, 1896

WHEN casting at a Spiegel furnace, a good deal of iron and manganese is always burned at the tap hole, giving a very hot flame and clouds of reddish fume, the hotter the furnace and the higher the percentage of manganese in the iron, the more sparks and fume. To protect themselves from these sparks the men often put a sheet iron screen over the run and tap holes. One day some water was accidentally spilled on this screen immediately after casting. It at once took the deep purple color of a permanganate solution; unfortunately the screen was upset and the solution spilled before I could secure any of it for further examination. At the time the furnace was working very hot, making a high grade spiegel and a basic cinder.

DISCUSSION.

Dr. Rosell called attention to the fact that potassium permanganate when heated to a red heat would decompose, and that the

[1] Read before the New York Section.

other permanganates behave in the same way. In fact the permanganates can only be made in the wet way. On the other hand, manganates are generally produced in the dry way, and they will stand a very high temperature.

If, therefore, a substance, after having been heated to the temperature of the blast furnace, would dissolve in pure water with the well known rich purple color of a permanganate solution, it seems almost certain that such a substance could not be a permanganate, but it could be a solution of a ferrate. It is, of course, also possible that the water used to dissolve the substance in question was not pure, but accidentally contained some acid, whereby, on dissolving, the manganate was converted into permanganate.

THE MANUFACTURE OF ACETONE AND OF ACETONE-CHLOROFORM FROM ACETIC ACID.[1]

BY EDWARD R. SQUIBB.

Received January 25, 1896.

JUST one year ago, January 11th, 1895, the writer read a paper before this Society upon "Improvement in the Manufacture of Acetone," and this paper was published in the Journal for March, 1895, page 187. The improvement claimed consisted in the use of acetic acid, instead of acetates, and in the use of a rotary still for the decomposition. The results given were obtained from a model apparatus on a table.

During the year that has elapsed since that paper was read, a large rotary still, twelve feet in length by two feet in diameter, has been set up, and this has decomposed in 126 hours about 1,700 pounds of absolute acetic acid, giving about ninety per cent. of the theoretical yield of acetone against about eighty per cent. in the small apparatus.

But the patentees of the processes for making acetone from acetates object to the use of this process and apparatus as being in conflict with their patents.

The acetone produced was converted into chloroform by the Watts (Seimerling) proportions of material in an apparatus described by the writer in 1857,[2] and used for many years ir making chloroform from alcohol, and this is also objected to.

[1] Read before the New York Section, January 10, 1896.

[2] *Ephemeris*, 4, [1], 71.

Under these circumstances it seems necessary to find out what has been done in the past upon this important subject, and what may be the relations of past work to the present conditions, and in this it is hoped the society may be interested.

ACETONE.

It is impossible to determine when or where acetone was first made and used.[1] According to the authority last given, after the time of Boerhaave in 1732, "the body was but little investigated until 1805, when Trommsdorff stated that on distilling acetate of potash or soda, a liquid was obtained which stands between alcohol and ether." In 1807 the Brothers Derosne in Paris[2] studied its properties; and in 1809 Chenevix[3] demonstrated that this substance was obtained by the dry distillation of any one of the acetates.

The correct composition of acetone was first given by Liebig[4] and Dumas.[5]

Further investigations by Kane, 1838, and by Chancel, Williamson, Chiozza, Freund, Wanklyn, and others, still more definitely established the sources, character and properties of acetone, and gave it a definite chemical and economic position so that its production or manufacture by the dry distillation of acetates was as well known as the production of alcohol by distillation from fermented sugars, as early as 1848, when Böttger refers to it as a market article in common use. Wackenroder,[6] in 1848, states that since acetone is quoted on the price lists at ten sgr. (Silbergroschen) per ounce, the preparation of chloroform from it is well worth recommending.

In "Handwörterbuch der reinen und angewandten Chemie herausgegeben von Dr. J. Liebig, Dr. J. C. Poggendorff und Dr. Fr. Wöhler—Redigirt von Dr. Hermann Kolbe, Braunschweig," 1842, Vol.. II, p. 1018, is the following (translated) statement:

According to Justus Liebig and Pelouze, the best thing to use

[1] See Wurtz' Dictionnaire de Chimie, 1873, 1, 31; Gmelin: Handbook of Chemistry, 1855, 9, 1; Roscoe and Schorlemmer: A Treatise on Chemistry, 1882, 3, [1], 568.

[2] *Ann. de Chim.*, **63**, 267.

[3] *Ann. der Phys.*, **32**, 191.

[4] *Ann. Pharm.*, **1**, 223.

[5] *Ann. Chim. Phys.*, **49**, 208.

[6] *Archiv. der Pharm.*, **53**, 273.

for the preparation of acetone is concentrated acetic acid, which in the state of vapor is conducted through a heated tube of glass, porcelain or iron, which for the sake of increasing surface, is filled with pieces of charcoal, and the products of decomposition are condensed in the usual way. The tube should be heated only to incipient redness; at a higher temperature only empyreumatic oils, combustable gases and charcoal are obtained as the products of the decomposition.

Besides the citations given, the literature on the preparation, properties and reactions of acetone is very copious and definite up to about 1853. After this date the papers published are comparatively few, leading to the inference that the substance had reached a definite position and gone into general use.

In a paper by Prof. Samuel P. Sadtler, Ph.D., "On Recent Improvements in the Methods for the Manufacture of Chloroform," published in *The American Journal of Pharmacy* for July, 1889, p. 321, the following statements are made:

"The old process of manufacture by the action of bleaching powder upon alcohol has given way to what is now termed the 'acetone' process. This is not, however, a new discovery. Liebig, in 1832, in following up his first account of the properties of the newly discovered "chloride of carbon" (chloroform) mentions that it can be gotten in very large quantities by the action of bleaching powder upon 'pyroacetic spirit' (acetone) as well as from alcohol. That alcohol has all this time been preferred to acetone as a material from which to prepare chloroform is due mainly to the fact that only in recent years has acetone been prepared pure in quantity, but also to the erroneous statement of Siemerling, quoted in the works of reference like Watts' Dictionary of Chemistry, that only thirty-three per cent. of chloroform could be gotten from acetone by the action of bleaching powder." . . . "The manufacture of a purer grade of acetone than that then in use for solvent purposes, having been begun in Germany in 1881, on the part of the 'Verein für chemische Industrie,' Liebig's old suggestion for the manufacture of chloroform from acetone was taken up by the 'Verein Chemischer Fabriken,' Mannheim, Germany, in the beginning of 1882, and a year later by the first mentioned company which made the acetone for both."

From these references it will be seen that the reactions involved in the production of acetone, and the constitution, character, properties and reactions of acetone had been long and well known prior to 1848, and that it had been made and utilized on a large scale prior to 1882; and further, that it had been produced both by the dry distillation of acetates, and by the wet distiilation of acetic acid, as a matter of open knowledge and practice.

This condition of the scientific knowledge of an important chemical substance throughout France and Germany—and throughout the scientific world—makes it very certain that the chemical industries, which depend upon such knowledge for their origin and progress in general, but do not publish their processes—availed themselves of this knowledge and of this chemical agent.

In June, 1886, application was filed in the U. S. Patent Office, and two years later, in July, 1888, Letters Patent No. 385, 777 were issued to Gustav Rumpf for the invention of a "New and Useful Improvement in the Manufacture of Acetone," and from the specifications and claims of this patent the following extracts are made:

"In making acetone by dry distillation of acetates, as acetate of lime, it has, before my invention, been thought possible to obtain only less than half the acetone."

"Dr. Herman Hager, in his Handbuch der pharmaceutischen Praxis, published in Berlin in 1882, states under the head of 'Acetone,' 'that it is possible to obtain an average yield from chemically pure acetate of lime of only fifteen per cent. of acetone, while the theoretical yield from chemically pure acetate of lime is thirty-four per cent.'"

"I have discovered that if the acetates are subjected for distillation to a low heat and approximately uniform temperature and the process extended over several hours, the yield of acetone will be greatly increased, and will approach very nearly the theoretical yield of any particular acetate, which in the case of good gray or commercial acetate of lime is about twenty-seven per cent. I have also discovered that in the process of subjecting acetates in a closed vessel to heat applied externally to the vessel

for distilling acetone from the acetates the desired slowness of distillation and uniformity of temperature may be secured by stirring the acetates so that all portions of the mass will be subjected to the heat resulting from direct contact with the bottom of the vessel, and by admitting free steam from time to time into direct contact with the acetates in case of any undesirable rise in temperature within the vessel."

"My invention consists in an improvement in the method of obtaining acetone from acetates by destructive distillation, consisting in subjecting the acetates in a closed vessel to slow destructive distillation at a low and approximately uniform temperature, and it is also well to stir the acetates during such distillation."

The claims are to—

"The improvement in the method of obtaining acetone from an acetate consisting in subjecting the acetate in a closed vessel to slow destructive distillation at a low and approximately uniform temperature."

This first broad claim is based, not upon the chemical reaction which was well known, nor upon the destructive distillation by heat, which was a well known process, but upon an improvement in the apparatus and management by which the yield of acetone was alleged to have been increased. But the evidence upon which the increase is claimed is an erroneous statement quoted from Hager—erroneous because it is hardly practicable through any ordinary degree of want of knowledge and skill to obtain so little as fifteen per cent. of acetone from acetate of lime.

The second claim is to a stirrer in its effects on the process. But a stirrer is a device so common in chemical processes that no such application of it can be considered original or new.

The third claim to the effect of the introduction of steam during the distillation is much better.

The fifth, sixth, seventh and eighth claims are to improvement in the process of purifying the crude acetone by means of lime, dilution and rectification, and these are but the steps common to all such operations.

It is upon this patent that infringement is charged, when it is

simply putting into use the very old process of making acetone by the destructive distillation of acetic acid in a rotary still as described in a paper on "Improvement in the Manufacture of Acetone," read before this New York Section of the American Chemical Society on January 11, 1895, and published in the Journal for March, 1895, p. 187, and in *An Ephemeris of Materia Medica, Pharmacy, Therapeutics and Collateral Information*, Vol. IV, No. 3, p. 1653.

The writer makes acetone by the destructive distillation of the watery vapor of acetic acid in a rotary still, in the presence of barium carbonate or pumice-stone or bone-charcoal, barium carbonate being preferred, because being a very heavy powder, a larger charge of smaller volume can be used.

The patentees claim only acetates as their material, but claim infringement by the use of acetic acid, because acetic acid is made from acetates, and acetates are made from acetic acid; and secondly, claim infringement on the ground that acetate of barium is first formed, and then decomposed in the rotary still, and therefore the process is really not a destructive distillation of acetic acid, but of barium acetate—one of the class of acetates claimed as secured to them by their patent, although in use for this purpose for so many years. That is, it is claimed that an acetate of barium is formed under conditions of temperature in which an acetate of barium cannot exist. Barium acetate decomposes at about 400° to 405° C. by an ordinary pyrometer. Acetic acid is best decomposed at about 500° to 525° C. by the same pyrometer, and yet it is claimed that at 500°C. barium acetate forms momentarily and then is instantly decomposed. That is, it is formed in an atmosphere in which it cannot exist for an instant, and in which acetic acid cannot exist.[1]

[1] Upon this point the patentees were very decided in the statement, based not only on their own experience, but also on the experience of their German correspondents, that if the barium carbonate was replaced by pumice-stone the amount of acetone obtained would be too small to have any commercial importance. This result had been confirmed to them by so many trials that at their suggestion, and in order to satisfy them that their results were not trustworthy, the following experiments were made after the above paper was written, but before it was published.

The large rotary still was emptied and cleaned out by sweeping, scrap-

But, quite apart from this, the chemical reaction by which acetone is produced, whether from acetates or from acetic acid, was well known for more than half a century before the date of this patent. What is really covered by the patent is certain specified and described apparatus and management whereby an improved yield is to be obtained from acetates, and from acetates only, for the apparatus and management are not at all applicable to the use of acetic acid, and are not used either in form or substance.

ACETONE-CHLOROFORM.

The history of acetone-chloroform dates distinctly back to 1832. In the *Annalen der Pharmacie*, *1832*, **21**, 198, Liebig describes the preparation of chloroform in large quantity, from given proportions of hypochlorite of lime, water, and alcohol, and he says the yield will be equal in weight to the alcohol used. He then goes on to say that chloroform may also be obtained in large quantity by treating acetone with hypochlorite of lime under the same conditions.

---

ing, and finally by sponging with water until it was quite free from any appreciable quantity of barium salt. It was then closed and run empty with a continuous feed of acetic acid for periods of three hours each, at the following temperatures, the rate of feeding, and the assaying for acid and acetone being approximate only, and only trustworthy by averaging.

At 300° C. 22.3 pounds of absolute acid was run in and
19.5 " " " " " received without any acetone or any evidence of decomposition of the acid, the 2.8 pounds of acid not accounted for being the normal charge of the apparatus.

At 350° C. 38.3 pounds of absolute acid was run in and
38.1 " " " " came through with no signs of any decomposition,—no acetone.

At 400° C. 36.1 pounds of absolute acid was run in and
29.9 " " " " " received undecomposed, leaving
6.2 " " " " decomposed, and this decomposed acid gave 97 per cent. of the acetone required by theory.

At 450° C. 35.1 pounds of absolute acid was run in and
18.5 " " " " " received undecomposed, leaving
16.6 " " " " decomposed, which apparently gave 112 per cent. of the acetone required by theory.

At 500° C. 41.4 pounds of absolute acid was fed in and
10.8 " " " " " received undecomposed, leaving
30.6 " " " " decomposed, which apparently gave 104 per cent. of the acetone required by theory.

At 550° C. 40.4 pounds of absolute acid was fed in and
5.1 " " " " " received undecomposed, leaving
35.3 " " " " decomposed, which apparently gave 82 per cent. of the acetone required by theory.

Liebig does not give the yield from acetone, but after giving the yield from alcohol as being equal in weight to the alcohol used, he says it is obtained in large quantity from acetone.

In 1835 Dumas and Peligot[1] state that when a solution of hypochlorite of lime is distilled with wood spirit there is obtained, as a matter of fact, some ordinary chloroform. The experiment is as easy as with alcohol or acetone.

Then a run of twenty-four hours was made at the last temperature, 550° C. to give opportunity for closer determinations of results.

321 pounds of absolute acid was fed in and
57.3 " " " " " received undecomposed, leaving
263.7 " " " " decomposed, which apparently gave 97 per cent. of the acetone required by theory.

The still was then opened, charged with 130 pounds of coarsely ground pumice-stone, and a parallel series of experiments made.

At 300° C. 41.8 pounds of absolute acid was fed in and
39.1 " " " " " received undecomposed, leaving
2.7 " " " " decomposed, which apparently gave 33.5 per cent. of the acetone required by theory.

At 350° C. 39.6 pounds of absolute acid was fed in and
34.8 " " " " " received undecomposed, leaving
4.8 " " " " decomposed, which apparently gave 87.5 per cent. of the acetone required by theory.

At 400° C. 41.8 pounds of absolute acid was fed in and
28.5 " " " " " received undecomposed, leaving
13.3 " " " " decomposed, which apparently gave 97 per cent. of the acetone required by theory.

At 450° C. 41.8 pounds of absolute acid was fed in and
13.0 " " " " " received undecomposed, leaving
28.8 " " " " decomposed, which apparently gave 95 per cent of the acetone required by theory.

At 500° C. 43.4 pounds of absolute acid was fed in and
8.8 " " " " " received undecomposed, leaving
34.6 " " " " decomposed which apparently gave 96.4 per cent. of the acetone required by theory.

At 550° C. 43.4 pounds of absolute acid was fed in and
7.4 " " " " " received undecomposed, leaving
36.0 " " " " decomposed, which apparently gave 100 per cent. of the acetone required by theory.

Then a run of twenty-four hours was made at the last temperature, 550° C., as a check upon the previous results.

345.5 pounds of absolute acid was fed in and
69.5 " " " " received undecomposed, leaving
276.0 " " " " decomposed, which apparently gave 104 per cent. of the acetone required by theory.

This last, and three other impossible results are as yet unexplainable, but they may be reasonably charged to the uncertainties in the use of an hydrometer and the iodoform process of assaying.

[1] *Ann. Chim. Phys.*, **58**, 15.

Liebig in his text-book[1] gives a formula and directions for the manufacture of chloroform from either acetone, alcohol, or wood spirit, and gives to acetone the leading place.

M. Bonnet[2], at a meeting of the Academy, says, "I have obtained in the distillation of equal parts of acetate of lime and hypochlorite of lime, in a stone retort, a very large quantity of chloroform, and far more easily than by the methods of preparation that are known.

Dr. Reich[3] proposed and used hypochlorite of sodium in place of hypochlorite of lime on account of the uneven amount of chlorine in the latter. He distilled together two pounds each of hypochlorite and acetate of sodium and received five to six drams of chloroform and twelve to fourteen ounces of acetone and water. This latter was again distilled with four to six ounces of hypochlorite, and again a considerable amount of chloroform and acetone was received. The last operation was repeated with a new portion of hypochlorite, and then the total amount of chloroform was eight to ten ounces, with still some excess of acetone for future operations.

Acetone when distilled with sodium hypochlorite yields chloroform in the proportion of four ounces of acetone to five to five and one-half ounces of chloroform.

Prof. Böttger[4] distilled together equal quantities of commercial bleaching powder and crystallized sodium acetate and obtained chloroform and acetone. Then he distilled the excess of acetone with a fresh portion of bleaching powder and had "great joy in seeing from this second operation a very considerable quantity of the purest chloroform distill over together with some acetone still undecomposed." The excess of acetone was again distilled with fresh bleaching powder and the process repeated until by three to four distillations all the acetone was used. The yield of chloroform being about four ounces to each pound of bleaching powder.

Chloroform made directly from acetone, which he says is at present, 1843, to be had in the market, is obtained in the propor-

[1] Traité de Chimie Organiques, 1, 576.
[2] L'Institut, No. 196 Februar, 1837.
[3] *Archiv der Pharmacie*, Zweite Reihe, *1848*, **55**, 65.
[4] Polytechnisches Notizblatt, *1848*, **3**, 1.

tion of one ounce and two drams of chloroform from one ounce of acetone.

Still in the year 1848 Prof. Heinrich Wackenroder,[1] one of the editors of the *Achiv*, says in substance: "The great practical interest in chloroform at the present time calls, first of all for a closer examination of the methods for making it. Therefore I have induced Mr. Siemerling to undertake, in my laboratory, some experiments relating to the preparation of chloroform which are in the most recent publications on the subject. Although these experiments have in no respect given the results which were hoped for, it nevertheless seems to be worth while to call attention to them for the sake of the future continuation of the subject."

Then follows the paper of Mr. V. Siemerling, and at page 26: "II. Preparation of Chloroform from Acetone."

"According to the statement of Prof. Böttger, one ounce of acetone, which has been mixed with hypochlorite of lime to a pasty mass, should give one ounce and two drams of chloroform. As this seemed to be an easy and advantageous method of preparation, some experiments were made with acetone procured from the factory of Trommsdorff, in Erfurt, but they did not accord with the statement of Böttger."

"In the first experiment (*a*) thirty grams of acetone were mixed with fifty grams of hypochlorite of lime and fifty grams of water and distilled. The chloroform was separated and rectified with concentrated sulphuric acid. The yellow chloroform thus obtained was again rectified from burnt lime when it had an empyreumatic odor—quantity not given."

In experiment (*b*) thirty grams of acetone, 120 of hypochlorite and enough water to make a pasty mass, were mixed and distilled. It is true much chloroform came over, but there was also much undecomposed acetone as well. It was repeatedly washed with water and rectified over calcium chloride, in which rectification there was a pretty large loss every time, but the number of times is not given. The yield was nine grams.

Experiment (*c*), since in both experiments undecomposed acetone distilled over the quantity (proportion) of hypochlorite was

[1] *Archiv. der Pharmacie, 1848*, 54, 23.

increased, and thirty grams of acetone to 150 grams of hypochlorite, with water, were mixed to a pasty mass, allowed to stand twenty-four hours, and were then distilled. The product contained much chloroform, but also undecomposed acetone; therefore it was put back into the retort with forty grams of fresh hypochlorite and again distilled. The chloroform thus obtained still contained acetone, from which it was purified by repeated washing with water, and then rectified over calcium chloride. The yield was ten grams of chloroform.

Another experiment (*d*) is given wherein twenty grams of acetone and sixty grams of hypochlorite were distilled together without water, but with unfavorable result, the yield being six grams of chloroform.

The specific gravity of the chloroform obtained from acetone, after repeated rectifications over calcium chloride was only 1.31, and it always contained some acetone; and the largest yield by Böttger's process was one-third of the acetone used. This differs considerably from his statement that one part of acetone yielded one and one-fourth parts of chloroform.

Siemerling then goes on to say, that if we assume with Liebig, that acetone is composed of one atom of acetyl oxide and one atom of methyl oxide, and explain in this way the formation of chloroform, from methyl oxide, it naturally follows that we must get less chloroform than the acetone used.

The sum of the elements of one atom of acetyl oxide $= C_4H_6O$ and one atom of methyl oxide $= C_2H_6O$ is equivalent to two atoms of acetone $= C_6H_{12}O_2$. In thirty grams of acetone there are therefore 11.8 grams of methyl oxide, which, since four atoms of methyl oxide consist of the same elements as two atoms of alcohol, can form 15.1 grams of chloroform, assuming that complete decomposition takes place.

According to the theory, half of the acetone used must be recovered as chloroform; but since in the practical manufacture of chemical products the quality prescribed by theory is never obtained, it should be considered a favorable result when one-third of the acetone used is obtained as chloroform, especially as the experiments were made only on the small scale.

From these experiments, it follows that the preparation of

chloroform from acetone is quite unfit for practical use. Were even the quantity of chloroform stated by Böttger as obtainable from acetone possible, it would have the disadvantage of being freed from acetone with very great difficulty.

The paper of Siemerling, from which the above abstract is made, seems to have received the endorsement of Wackenroder, although it controverts the statements of both Reich and Böttger, and it may be from his high authority as much as from the paper itself that the results seem to have been accepted and quoted by Gmelin,[1] Watts,[2] and other reference authorities, and the influence of the publication seems to have been, so far as the literature of the subject goes, to prevent or obstruct the acetone process for many years. As it was so long and so well-known, manufacturers may have been, and probably were using the process privately, but up to 1881–1883[3] very little information on the subject is found. Still the work and the conclusions of Siemerling must have been known to be grossly erroneous by every one whose interest it became to try them. Calculations would show to anyone that when ordinary acetone and bleaching powder were used the proportions required are about one to ten, or about double the largest proportion of hypochlorite used by Siemerling, and the resulting chloroform should be about double the weight of the acetone used; and many who preceded Siemerling knew better than he how to save and utilize the great excess of acetone, or deficiency of hypochlorite taken.

But the Siemerling results were very faulty and very misleading in other respects. The present writer having learned from all the work of the past on the subject, that any excess of acetone used could be easily recovered and used again, added to this knowledge from his own experience the fact, that, where an excess of acetone was taken, the hypochlorite was more economically and more promptly utilized, and the resulting chloroform was cleaner. Having gained from the Siemerling process this step the writer was prepared to try that proportion and process critically, and he found that, as a table experiment, it was

[1] Handbook of Chemistry, Vol. VII, 346.
[2] Dictionary of Chemistry, *1883*, I, 918.
[3] Sadtler, *Am. J. Pharm., July. 1889*, 321.

quite impracticable by any reasonable degree of mismanagement to obtain so low a result. In two fairly careless trials from thirty grams of ninety-six per cent. acetone the yield of chloroform was twenty-three grams in one case and thirty-two grams in the other, instead of Siemerling's ten grams. In larger trials of his proportions up to 280 pounds of absolute acetone to one cask of 1400 pounds of thirty-three per cent. bleaching powder in one charge the yield was not less than 200 pounds of chloroform, and about 130 pounds of recovered acetone, thus proving conclusively the gravity of the unaccountable errors of the Siemerling work, and showing a basis for the mischief done by this bad work.

Looking back from this later day at the authoritative way in which these mistakes and misstatements of Siemerling were published and quoted, it is easy to see that nothing could be better adapted to obstruct or prevent any increase in the general production of acetone-chloroform, and to confine its productions to those manufacturers who were using the process secretly.

One of the definite evil consequences of this Siemerling paper was the adoption of its erroneous results as the basis of the following patent.

On June 23, 1886, Gustav Rumpf applied for a patent, and on July 5th, 1888, patent No. 383,992 was issued to him for the invention of "A New and Useful Improvement in the Manufacture of Chlroform from Acetone," of which the following is a specification: "The essential feature of this invention is based on the discovery that acetone when treated in the proper way with a hypochlorite—for example chloride of lime—will yield a larger quantity of chloroform than has been heretofore known. Watts, in his Dictionary of Chemistry, edition of 1883, **1**, 918, says that the manufacture of chloroform from acetone cannot usefully be carried out, not only because the price of acetone is too high, but particularly because acetone yields about thirty-three per cent. of its own weight of chloroform when it is treated with chloride of lime. Watts distilled thirty grams of acetone with 150 grams of chloride of lime, and rectified the watery distillate with forty grams of chloride of lime. I have discovered a method whereby it is possible to obtain a yield of chloroform from ace-

tone very much greater than that obtained by Watts. I have found that the reaction may be made to take place in such a way that one equivalent of acetone will yield one equivalent of chloroform by volume, or about 180 per cent. by weight, and the advantages of my invention may be secured in a greater or less degree by properly employing with about fifty-eight pounds of acetone more than 300 pounds of good chloride of lime. The best results and greatest yield of chloroform can, as I have found, be obtained by the use of, say, fifty-eight pounds of acetone to at least 600 pounds of a good chloride of lime containing about thirty-five per cent. of available chlorine, and in proportion if the chloride of lime is poorer. The yield of chloroform will then be from 150 per cent. to 180 per cent. of the weight of the acetone employed instead of about thirty-three per cent.

Then follow claims for invention of diluting the acetone and of introducing it periodically during the process—of introducing it below the surface of the solution in the still—of the use of a mechanical stirrer, and of the use of a still and condenser which are described and figured.

The basis upon which this patent rests, for its reason to be, is the quotation from Watts' Dictionary. Watts quotes the process from *Gmelin's Handbook*, and Gmelin quotes it from *Siemerling's Paper* in the *Archiv der Pharmacie*, *1848*, **54,** 26. Now, as the paper and quotations are grossly erroneous, and as writers of preceding papers publish results that approximate those of the patent, it might reasonably be asked what is the value of the patent. But the present writer, while intending to make acetone-chloroform, very earnestly desires to avoid all question in regard to the validity of this patent, and therefore uses the Watts (Siemerling) process, which is outside the limit claimed by the patent, with an entirely different apparatus and management described by him in 1857, and republished in *Ephemeris*, **4**, [1] 71.

It is proposed to use charges of 280 pounds of absolute acetone to 1,400 pounds of thirty-five per cent. bleaching powder, one to five—to pass the resulting chloroform through scrubbers, then distil it through water, then distil it from a small portion of bleaching powder, then pass it through sulphuric acid scrubbers,

and finally rectify it in three fractions, the large middle fraction being accepted, and the others being worked over.

A part of the great excess of acetone taken in the one to five proportion is recovered by continuing the distillation after the chloroform is all over. Another part is recovered in the wash water from the scrubbers and the distillation, and the small remainder is decomposed by the small proportion of bleathing powder. the total amount recovered being practically not far from the total excess.

To this recovered acetone, carefully assayed, new acetone is added to make up the 280 pounds for the next charge.

The patentees were invited to see this apparatus and process in order to convince them that there is a strong desire to avoid any color of infringement by taking the Siemerling proportions which are excluded from their patent. But they took the ground that this was a mere evasion, or getting round their patent by using the excess of acetone over again, and could not be made to see that this, if objectionable, is so by defect in the equity of the patent, and is a proceeding that ante-dated the patent by many years. And finally they covered everything by claiming that the patent secured to them the sole right to make chloroform from acetone in the United States, thus claiming a reaction that had been well known for more than fifty years.

As to the reasons why large manufacturers of chloroform did not avail themselves earlier of the acetone process, the first answer is that it is probable that many of them, in Germany, at least, did so secretly as soon as acetone became cheaper than alcohol.

But, as to other more positive reasons, the writer, as having been for many years a large manufacturer from alcohol and as having, with all other makers, given up the manufacture rather than contest this patent, can only speak for himself. He for many years doubted the identity of alcohol and acetone-chloroform, and doubted whether the latter was as easily purified for use as the former, so that when chloroform was offered to him at so low a price as to insure that it was made from acetone it was refused. Chloroform has always been a most important agent, and during the earlier part of its career the numer-

ous fatalities from its use were charged to its impurities, so that the alcohol process was adhered to until the identity of the products from alcohol and acetone was fully proved,—not only chemically, but also by surgical experience of considerable duration. Then as time passed and the subject came up for research and reconsideration, the Siemerling results came up also and settled the question against acetone.

Finally Dr. Gustav Rumpf, a German, and an employé for some years in an acetone-chloroform manufactory in Germany, where there is no patent, came to this country, took out these patents and assigned them to the present holders, so that now for the past seven years or more any one making acetone-chloroform in this country by processes that had been free and largely used in Germany for many years, was liable to prosecution for infringement.

Having any general knowledge of the history of acetone and acetone-chloroform, it is difficult to understand how such patents could be issued that would claim to control the proportions of well known chemical materials in long known chemical reactions. But such patents were issued, and, therefore, command respect. That the processes were not used earlier in this country may be charged chiefly to the endorsements of the Siemerling paper; and that the patents appear to have been so long acquiesced in is due to the circumstance that any one who might contest them would do so at great cost of money, time and annoyance in defensive litigation, whice, if successful, would secure the benefits equally to many manufacturers, and to the public in lower prices of the products, whilst the contestant would bear all the costs.

In seeking new outlets for acetic acid the writer determined to convert the acid into chloroform, and determined also to respect these patents. In the intermediate step of making acetone, acetic acid was used, not to evade the patents, but because by its use the impurities of the crude acetates of lime were avoided, and a larger yield of better acetone was obtained. In the use of acetic acid instead of the acetates of the patent an entirely different apparatus and management are required and used, and if the patent did not exist the writer would not use either its appa-

ratus or management, but would prefer the rotary still and the continuous process.

With regard to the other step wherein the acetone is converted into chloroform, this is accomplished by a reaction that was long and well known before the date of the patent, and the proper portions of the material required for the reaction were easily obtainable by calculation, and this knowledge also ante-dated the patent. The patent then simply covers a specially devised and described apparatus and management which the writer does not use and does not want to use even if they were not patented, but much prefers his old form of apparatus and management described in 1857, and used for many years in making alcohol chloroform. And the successful use of this apparatus and management for acetone chloroform is simply in accordance with the statement of Liebig, in 1832, that acetone could be successfully used under the same conditions as alcohol.

PYRIDINE ALKYL HYDROXIDES.[1]

By A. B. Prescott and S. H. Baer.

Received January 27, 1896.

THE HYDROXIDES OF QUATERNARY NITROGEN BASES IN GENERAL.

TETRAMETHYL and tetraethyl ammonium hydroxides were well described by their discoverer, A. W. Hofmann,[2] in 1851. Their crystallization in a vacuum, their behavior as alkalies in reaction with the metallic salts, and their conversion to carbonates upon exposure to the air were then set forth. Various quaternary bases of mixed formation from methyl, ethyl, amyl and phenyl were made by Hofmann at the same time. The tetrapropyl ammonium hydroxide was first described by Roemer, in 1873.[3]

The decomposition of quarternary ammonium hydroxides by heat was reported upon by A. W. Hoffman, in 1881,[4] also by Lawson and Collie, in 1888.[5]

1 Read at the Cleveland meeting.
2 Phil. Trans., *1851*, (2), 357; *Ann. Chem.* (Liebig), **81**, 253; **86**, 292; **91**, 33.
3 H. Roemer, *Ber. d. Chem. Ges.*, **6**, 786.
4 *Ber. d. Chem. Ges.*, **14**, 494.
5 *J. Chem. Soc.*, 53, 634.

Pyridine ethyl hydroxide was mentioned by Anderson in 1855.[1] The methyl hydroxide was reported upon by A. W. Hofman in 1881[2]. In this relation are to be considered the numerous products of the action of alkalies upon the alkyl iodides of pyridine and quinoline, obtained by Claus and by Decker, mostly in 1892 and 1893.[3]

PYRIDINE PROPYL HYDROXIDE.

Pyridine propyl iodide, prepared as stated in another paper from this laboratory,[4] was treated with moist recent silver oxide, shaking for some time in a flask, keeping down the temperature. The silver oxide for all this work was made by precipitating silver nitrate with potassium hydroxide and washing the precipitate until the washings give no color reaction with hematoxylin, to ensure the removal of the alkali. Silver oxide is sufficiently soluble in water for its solution to color litmus or phenolphthalein.

On filtering out the silver iodide, the solution of pyridine propyl hydroxide was colorless, and was found to precipitate salts of lead, silver, copper, iron, aluminum, chromium, cobalt, and nickel, an excess of the hydroxide dissolving only the precipitates of lead and of aluminum, these reactions agreeing with those of fixed alkalies. In parallel treatment with pyridine it was found not to precipitate these salts, the only apparent reaction with any of them being a blue color with the copper salt. The solution of pyridine propyl hydroxide gave the alkaline reaction with the following indicators: litmus, phenolphthalein, brazil wood, cochineal, hematoxylin, and methyl orange. Pyridine gives an alkaline reaction with all these indicators except phenolphthalein and hematoxylin, these two being capable of use in a volumetric acid estimation of the pyridine propyl hydroxide in presence of pyridine.

On heating the solution of the pyridine propyl hydroxide it acquires a red color, and the solid residue by evaporation has a black color, dissolving in water again as a red solution.

[1] *Ann Chem.* (Liebig), **94**, 361.
[2] *Ber. d. chem. Ges.*, **14**, 1498.
[3] *J. prakt. Chem.* (2), **46**, 106, **47**, 208, 426: *Ber. d. chem. Ges.*, **25**, 3326.
[4] A. B. Prescott, this Journal, **18**, 92.

PYRIDINE ISOPROPYL HYDROXIDE.

This base was prepared in the same manner as the normal propyl hydroxide, and it was found to give the same reactions with indicators and with metallic salts, as well as the same color when evaporated.

The isopropyl[1] base has been elsewhere stated by one of us to form a more stable iodide, of higher melting point and lower solubilities, than the iodide of the normal propyl base, and the isopropyl hydroxide has been taken, instead of the normal propyl-hydroxide, in our further experimentation.

The production of the pyridine isoyropyl hydroxide, in solution, can be made quantitatively complete as a base saturating sulphuric acid. Weighed portions of the iodine were converted to hydroxide in solution, with due precautions against loss, and the liquid titrated with tenth normal solution of sulphuric acid, using hematoxylin and cochineal, respectively, as indicators, and titrating back to the end reaction with tenth normal solution of potassium hydroxide. The hematoxylin was used in a titration to avoid interference by free pyridine, should this be present as a product of decomposition, as it does not color this indicator. The cochineal was used because it is an indicator of special delicacy for titration of pyridine alkyl hydroxides.

The results were as follows: the percentage of hydroxide *calculated* from the iodide being 55.82, the percentage of hydroxide *found* by titration with cochineal was 55.25 and 55.88, with hematoxylin it was 55.6 and 55.7

The solution of pyridine isopropyl hydroxide, on evaporation to dryness, yields a black residue, which is permanent, so that after standing three months it gives with metallic salts all the reactions of the hydroxide. The color in solution changes to red, like that of the normal propyl hydroxide. By exposure to the air it is steadily converted to the carbonate.

When the solution was treated for some time with carbon dioxide gas, then evaporated to dryness, the residue was found to bear the composition of a normal carbonate of the enivalent base. This composition was determined from the amount

[1] Pyridine Alkyl Iodides, this Journal, 18, 93.

of carbon dioxide recovered in an absorption train, in ratio to the weight of iodide taken for conversion to hydroxide. The calculated weight of carbon dioxide being 14.44 per cent. of $(C_5H_5N.C_3H_7)_2CO_3$, there were obtained 14.99, 14.88, and 14.79 per cent. of carbon dioxide. In other trials the carbonation was incomplete, reaching only to 9.3, 9.47, and 10.1 per cent.

In no case was the full quantity of pyridine isopropyl hydroxide obtained in weight of the dry residue, although the evaporation was conducted under different conditions, in vacuum, in a stream of dry air, and in a stream of dry hydrogen. In the case of the carbonate, the weight of the residue did not fall below the theoretical quantity. As hydroxide the weight of the residue always fell a good deal short of the full quantity.

Pyridine isopropyl platinum chloride, perfect in proportions, was prepared from the black residue left on evaporation of the water solution of pyridine isopropyl hydroxide, by treatment in the usual manner. The black mass was dissolved in alcohol, treated with hydrochloric acid and platinum tetrachloride, and the crystalline precipitate fitted for analysis. Fine crystals were obtained, not melting below temperatures which cause decomposition.

	Calculated for $(C_5H_5N.C_3H_7Cl)_2PtCl_4$.	Found. I.	II.	III.
Platinum	29.95	30.08	30.48	30.29
Chlorine	32.58	32.50	....	32.39
Ratio of Cl to Pt	100:108	100:108	....	100:107

Pyridine isopropyl sulphate, the normal salt, was also prepared in fine crystals, by adding sulphuric acid to the hydroxide.

In various efforts to obtain the pure hydroxide in the solid state, crystalline or amorphous, vacuum desiccation, freezing temperature, formation in absolute alcohol solution, and other agencies were successively tried, without success. Crystals were not obtained, and the residue was always dark colored. Evaporation in a stream of dry hydrogen yielded a residue of the same weight as that obtained by evaporation in a stream of dry air.

These results, so far, may be summarized as follows:

Pyridine isopropyl hydroxide remains in aqueous solution for

a time without decomposition or loss in any way. The residue by evaporation of this solution, in air, or hydrogen, or vacuum, contains a considerable portion of the unchanged hydroxide, along with certain decomposition products not yet determined. The normal carbonate of this base, its normal sulphate, and its platinum chloride are easily prepared and preserved.

UNIVERSITY OF MICHIGAN.

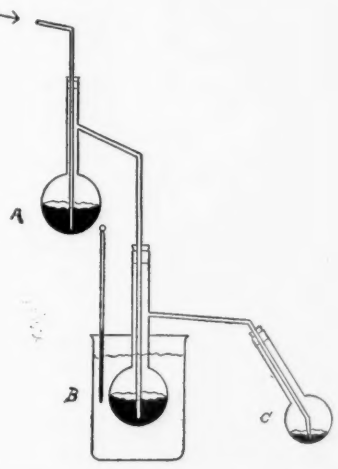
ON THE REDUCTION OF SULPHURIC ACID BY COPPER, AS A FUNCTION OF THE TEMPERATURE.

BY LAUNCELOT ANDREWS.

Received January 9, 1896.

THE object of the experiments described in this paper was to determine whether there duction of sulphuric to sulphurous acid by copper take place at a higher or a lower temperature than the incipient dissociation of the former compound into water and the acid anhydride.

The sulphuric acid employed was the ordinary pure product, containing 98.4 per cent. of sulphuric acid. The apparatus illustrated in the adjoining figure was used.



The method resorted to was to heat the copper with the sulphuric acid (in flask *B*) gradually in a sulphuric acid bath, while passiug a dry current of air of carbon dioxide through it. The escaping gas was then tested (in flask *C*) by suitable reagents, to be described, for sulphuric and sulphurous acids respectively. Flask A contained concentrated sulphuric acid at the ordinary temperature (25° C.) to dry the gas, which was passed at the rate of about eighty bubbles per minute, except when otherwise men-

[1] Read before the Iowa Academy of Sciences, January 2, 1896.

tioned. The importance of securing absence of dust being recognized, the whole interior of the apparatus was washed with boiling concentrated sulphuric acid, then with water and dried in dustless air.

Experiment I.—Flasks *A* and *B* were charged with concentrated sulphuric acid and *C* with a solution of barium chloride. Air was drawn through the whole in a slow current for fifteen minutes. The solution *C* remained clear. *B* was now very slowly heated, while the current of air was maintained. Before the bath reached 70° C. there appeared in *C* a faint turbidity of barium sulphate which, at the temperature named, became distinct, but at 60° C. the solution remained unchanged even after passing the air for a long time. Hence, sulphuric acid of the given concentration begins to give up sulphur trioxide, that is, it begins to dissociate at a temperature lying between 60° and 70° C. and nearer to the latter.

Experiment II.—The apparatus was charged as before, with the addition of pure bright copper wire in *B* and with highly dilute iodide of starch in *C* instead of barium chloride. After passing air for several hours at the ordinary temperature, much of the copper had gone into solution and anhydrous copper sulphate had crystallized out, but the iodide of starch, made originally very pale blue, retained its color.

This shows that in the presence of air sulphuric acid is attacked by copper at ordinary temperature, but without reduction of the acid. The reaction must take place in accordance with the equation,

$$2Cu + O_2 + 2H_2SO_4 = 2CuSO_4 + 2H_2O.$$

Experiment III.—This was like the last, except that the apparatus was filled with carbon dioxide[1] and a current of this gas was substituted for air. The copper was not attacked and the starch iodide was not decolorized. The temperature of *B* was now slowly raised, and when it reached 90° C. the solution in *C* was bleached.

In a similar experiment a solution of dilute sulphuric acid colored pale straw yellow with potassium bichromate was used as an indicator for sulphurous acid in *C*. In this case the change

[1] Freed from oxygen by bubbling through chromous acetate.

of color did not occur until the temperature had risen to 108° C., the indicator being, as might be expected, less sensitive than the other.

Experiment IV.—This resembled III, except that a reagent for both sulphuric and sulphurous acid was used in *C*. This reagent was prepared by slightly acidifying a semi-normal solution of barium chloride with hydrochloric acid and then adding enough potassium permanganate to render the solution pale rose color. This indicator is capable of showing the presence of considerably less than 0.01 milligram of sulphurous acid.

When the temperature of the bath had reached 70°C. the solution in *C* was distinctly turbid with barium sulphate, but its color was unaltered. At 86° it began rather suddenly to bleach, and at 87° it was colorless. Special care was taken in filling *B* not to get any sulphuric acid on the neck or sides of the flask. A repetition of this experiment gave identical results, the gas being passed at the rate of two or three bubbles per second.

The conclusions to be drawn from this investigation are:

First. That the dissociation[1] of sulphuric acid of 98.4 per cent. begins to be appreciable at a temperature somewhat below 70°, which may be estimated at 67° C.

Second. The reduction of sulphuric acid by copper does not begin below 86°, that is, not until the acid contains free anhydride.

The assertion made by Baskerville[2] that sulphuric acid is reduced by copper at 0° is, therefore, incorrect. He appears to have based the statement, not on any demonstration of the formation of sulphurous acid, but solely on the formation of copper sulphate, which occurs as I have shown[3] in consequence of the presence of air. I believe that a repetition of his experiments under conditions securing entire absence of oxygen can but lead him to a conclusion different from that to which he now adheres.

[1] The appearance of barium sulphate in *C* can not be accounted for by an assumed volatility of sulphuric acid as such, but only by its dissociation, because volatilized sulphuric acid would condense in the cold tube between *B* and *C*, since it has been shown that the acid was not appreciably volatile at the temperature of the latter. Hence only the anhydride could pass this cold tube and appear as sulphuric acid in *C*.

[2] This Journal, 17, 908.

[3] Traube has shown the same thing for dilute sulphuric acid. *Ber. d. chem. Ges.*, 18, 1888.

The fact adduced by him that, under certain conditions, cuprous sulphide may be formed by the action of the metal upon sulphuric acid does not allow any conclusions to be drawn respecting the presence of "nascent" hydrogen, since it may be explained perfectly well, either by the direct reducing action of the copper or by Traube's theory, which is backed up by *almost* convincing evidence.[1]

Stannous chloride will reduce sulphuric acid with formation of hydrogen sulphide, sulphurous acid and free sulphur: an analogous reaction in which the assumption of "nascent" hydrogen is inadmissible.

I hope to complete before long another series of experiments, now under way, which will form in a future communction a further contribution to the subject of the present paper.

THE OXIDATION OF SILVER.

By Charles E. Wait.

Received January 17, 1896.

IN a former paper[2] I had occasion to call attention to the large amount of silver present in a sample of bismuth litharge from a western smelting and refining company. The silver in this instance estimated in the metallic state was 2.94 per cent.

There was some doubt expressed as to the condition in which the silver existed, it being usually reported in the metallic state. Upon investigation it was found, as was shown in the paper referred to, that the silver did not exist wholly in the metallic state, but partly in another form, probably the oxide.

The conclusions reached at that time were based upon the following experiments:

1. A weighed sample of the litharge was boiled in acetic acid for about half an hour, the solution was filtered, and the filtrate gave no reaction for silver.

2. Same as above, but with continued boiling, the filtrate gave no reaction for silver.

3. A sample was placed in cold acetic acid, kept there for half an hour, then heated to boiling, the solution was filtered, the lead was precipitated, and in the filtrate silver was found to exist, corresponding to 19.25 per cent. of the silver in the litharge. Other determinations gave closely agreeing results, and

[1] Moritz Traube, *loc. cit.* and *Ber. d. Chem. Ges.*, 18, 1877.

[2] Trans. Am. Inst Min. Eng., 15.

it is interesting to note that the residue contained grains of metallic lead, or argentiferous lead.

I have placed the following interpretations upon the above results:

In Nos. 1 and 2 if any silver in any form was dissolved in the acetic acid, it was in turn reprecipitated by boiling, in the presence of metallic lead.

In No. 3 the silver dissolved, did not in all probability exist in the metallic state; and in this case was not precipitated by the lead, or argentiferous lead, the solution being brought merely to the boiling temperatnre.

I have been led to the above interpretations by showing that neither metallic silver reduced to fine subdivision by mechanical means, nor silver freshly prepared by zinc from silver chloride is soluble in acetic acid, while argentic oxide is soluble in that acid; and a solution of silver oxide in acetic acid was precipitated completely by metallic lead upon boiling.

If the oxides are decomposed at a temperature of 300° C.,[1] or less,[2] how may we account for the existence of this substance in a product so highly heated as the litharge from the refining furnace?

Berthier[3] has observed that lead may be oxidized by oxide of copper, when melted together, and further consideration of the subject shows that certain metals may be oxidized by being melted with an oxide of another metal, this oxidation depending in all probability upon the excess of the oxide present. Silver does not appear to be oxidized by oxide of copper if the results in experiment No. 18 are trustworthy.

According to Fournet's experiments[4] silver is not an exception to the metals to which litharge gives up a part of its oxygen when fused with them for a considerable time.

While it is true that in the process of cupellation there is a loss of silver due possibly to oxidation, yet I do not find any losses even in the most exaggerated cases at all comparable with the percentage of silver oxide which I have been able to produce by a simple, yet possibly new, method.

It seemed to me an interesting problem to astertain, if possible, the condition under which silver may be oxidized at a high

[1] Roscoe and Schorlemmer, Vol. II, Part I.
[2] *J. Chem. Soc.*, 65. 316.
[3] Crookes and Rohrig, Metallurgy.
[4] Erdman's Journal.

temperature, and the conditions under which the oxide of silver, if thus formed, would remain as such.

Some interesting work has been done along a similar line,[1] that is, a study of those oxides which are stable at high temperature, and those which are decomposed, but under neither head does silver seem to have been discussed.

So few observations have been made along this exact line, as far as I have seen, that I have been induced to make some investigations with a view to throw light upon the subject, if possible.

The general method of conducting the experiments, I will briefly state as follows: Metallic silver in minute subdivision was incorporated with one of the several bodies mentioned below; this mixture was put in a cupel of bone ash, or in a scorifier, and then placed in a muffle of an assay furnace and subjected to an oxidizing heat.

After this operation the mass was removed to a mortar, pulverized, then digested with acetic acid to boiling, the solution was filtered; in case a lead compound had been used, the lead was removed by sulphuric acid, and hydrochloric acid was then added. The silver chloride thus formed was filtered, dried, and wrapped in least pure lead foil and then carefully compelled.

There was thus obtained the silver, which was converted to argentic oxide,—at least I assume it to be such,—and it is interesting to note that the amount of silver converted to oxide, and tabulated below, shows a very great range, in fact from only a trace to as much as thirty-nine per cent. of the silver used.

This variation seems dependent upon a number of conditions, namely: the body with which the silver was mixed, duration and condition of heat, whether low, medium, or high temperature. As I did not use a pyrometer to ascertain the temperature during these experiments, I have thought it desirable to indicate the degree of heat approximately by such terms as "low," "medium," and "high," referring to the condition of the heat as usually obtained in the muffle in the assay of silver.

I append herewith several tables of experiments and results:

[1] *J. Chem Soc.*, April, *1894*.

TABLE A.

No. experiment.	Ag in gram.	Heated with	Time of heat	Condition of heat.	Per cent. Ag as Ag_2O.
1	0.5	2.5 grams MnO_2.	60 min.	medium	9.40
2	0.5	5.0 " MnO_2.	60 "	"	7.78
3	0.5	2.5 " Fe_2O_3.	60 "	"	none.
4	0.5	2.5 " Bi_2O_3.	60 "	"	"
5	0.5	2.5 " ZnO.	60 "	"	"
6	0.5	2.5 " $CaCO_3$.	60 "	"	"

From the above it will be seen that silver oxide was produced, and remained as such where manganese dioxide was used and in no other case; it would also seem that this oxide was made at the expense of the manganese dioxide and not by atmospheric oxidation, nor does it seem to have been produced in experiment 3, (certainly not remaining as such) assuming the possible conversion of Fe_2O_3 to Fe_3O_4.[1]

TABLE B.

No. experiment.	Ag in gram.	Heated with	Time of heat.	Condition of heat.	Per cent. Ag as Ag_2O.
7	0.5	7.5 grams MnO_2.	30 min.	medium.	34.16
8	0.5	10.0 " MnO_2.	30 "	"	18.84
9	0.5	3.0 " $CaCO_3$.	60 "	"	none.
10	0.5	3.0 " Fe.	60 "	"	"

The above results show that silver oxide was produced in the presence of manganese dioxide only; that less duration of heat than in Table A gives the amazing large per cent. of that oxide, and it furthermore seems that the oxide produced is not in proportion to the manganese dioxide used, but the reverse condition is generally seen in each set of experiments.

TABLE C.

No. experiment.	Ag in gram.	Heated with	Time of heat.	Condition of heat.	Per cent. Ag as Ag_2O.
11	0.5	1 gram MnO_2.	2.5 min.	high.	32.24
12	0.5	2 grams MnO_2.	2.5 "	"	34.28
13	0.5	2 " MnO_2.	20 "	"	11.72

The above experiments show, other conditions being the same, the longer the duration of the heat the less oxide there is produced.

[1] *J. Chem. Soc.*, 65, 313.

TABLE D.

No. experiment	Ag. in gram.	Heated with	Time of heat.	Condition of heat.	Per cent. Ag as Ag_2O.
14	0.5	5 grams PbO.	10 min.	medium.	38.85
15	0.5	4 " PbO_2.	10 "	"	35.11
16	0.5	2 " BaO_2.	5 "	"	12.28
17	0.5	7 " BaO_2.	10 "	high.	2.04
18	0.5	4 " CuO.	12 "	"	none.

In Nos. 14 and 15 the mixtures were placed in scorifiers, and covered with ten grams of lead oxide.

In Nos. 16 and 17 the mixtures were placed in cupels and covered with two grams of barium dioxide.

It is interesting here to notice that barium dioxide serves as an oxidizing agent; that the amount of silver oxide produced decreases probably both with increase of time and temperature.

Although lead dioxide may readily give up a part of its oxygen and thereby be converted into a lower oxide, yet the amount of silver oxide produced was no greater than with lead oxide alone; this is an interesting illustration of the property of lead oxide to serve as a possible carrier of atmospheric oxygen, producing silver oxide in a manner similar to that of the two bodies, manganese dioxide and barium dioxide, liberating oxygen. In the case of lead oxide, No. 14, if dissociation is not possible[1] even at so high a temperature as 1750° C., it seems most reasonable to account for its peculiar oxidizing action, as mentioned above; *viz.*, as a carrier of atmospheric oxygen. Although copper oxide has been shown to yield up a part of its oxygen at 1500° C., yet I find no evidence of silver oxide existing in experiment 18 in the remaining ignited mass.

TABLE E.

No. experiment.	Ag_2O in gram.	Heated with	Time of heat.	Condition of heat.	Per cent. Ag as Ag_2O.
19	0.5 Ag_2O.	5 grams MnO_2.	60 min.	medium.	36.4
20	0.5 Ag_2O.	3 " Fe.	60 "	"	0.3
21	0.5 Ag_2O.	3 " $CaCO_3$.	30 "	"	0.2

In Table E a variation was made in the nature of the experiment. Freshly prepared silver oxide was used; while this oxide was completely decomposed upon being heated gently upon a porcelain lid, yet in No. 19 where manganese dioxide

[1] *J. Chem. Soc.*, 65, 316.

was used, it will be seen that 36.4 per cent. of this silver oxide completely escaped decomposition.

The above results, in connection with others along a similar line, have induced me to believe that attention has not heretofore been directed to the ease with which silver may be oxidized by lead oxide, and particularly by substances which give up a part of their oxygen upon gentle ignition, such as manganese dioxide and barium dioxide. It is not then reasonable to assume that certain losses, or irregularities in the treatment of silver and its compounds, may be due to this cause?

UNIVERSITY OF TENNESSEE.

THE DETERMINATION OF THE SOLID FAT IN ARTIFICIAL MIXTURES OF VEGETABLE AND ANIMAL FATS AND OILS.

BY J. H. WAINWRIGHT.

Received February 1, 1896.

IT will be readily conceded by most analysts that there is no subject in analytical chemistry presenting more difficulties than the examination and analysis of the fixed oils and fats. This is especially true in the case of mixtures of oils of different origin, and there is probably no problem more difficult to solve in most cases than the analysis of such a mixture when even approximately correct quantitative results are required.

It is only within a comparatively recent period that the investigations of the chemist have been especially directed to this branch of research as formerly the character and identity of a sample of unknown origin was chiefly, but very doubtfully established by means of obscure color reactions and one or two simple determinations, such as specific gravity, melting point, etc.

At present, however, the investigations of many learned chemists have shown that determinations of the chemical and physical properties of a sample, such for example as the combining weight of fatty acids, the percentage of iodine the sample will absorb, the percentage of volatile fatty acids, etc., will yield results by which may be established, in most cases with reasonable accuracy, the fact as to whether it is a simple oil or fat, such as olive, linseed, lard, butter, etc., and if so its iden-

tity and quality; or, if adulterated, to determine with a fair degree of accuracy the character and probably extent of adulteration. This is especially the case when a mixture consists of but two oils or fats, one of which is known, in which case a few quantitative determinations will usually enable the analyst to readily astertain its approximate composition.

If a sample, however, consists of a mixture of *more* than two oils or fats, any statement of its composition calculated from the results of such determinations as above mentioned would be of extremely doubtful accuracy in any case, even if one of the constituents were known, and even then it would be at best but a broad approximation owing to the variations in chemical and physical properties exhibited in different specimens of the same kind of oil.

Some years ago samples of compound lard for export were submitted to the United States Laboratory for analysis with a view to determining the relative proportions of its constituents in order that the claim of the exporter for "drawback" of duties paid on one of its constituents might be verified.

This "compound lard" or "lard compound" has in recent years become an important article of commerce and consists essentially of cotton-seed oil and oleostearin made from beef fat mixed in different proportions; and sometimes containing a small percentage of genuine lard. Its composition is variable according to the brand and particular formula by which compounded, but is generally about as follows:

	Per cent.
Oleostearin	20 to 30
Cottonseed oil	70 to 80
or	
Oleostearin	18 to 30
Lard	10 to 20
Cottonseed oil	65 to 75

In the first case determinations of the properties of the sample would disclose its composition with reasonable accuracy, but in the second case considerable time was spent, I might almost say wasted, in making a long series of these determinations, both on the samples themselves and on mixtures made in the labora-

tory in accordance with the formula for comparison, without arriving at any satisfactory conclusions, until finally a very simple method for the analysis or rather assay of these "lard compounds" was devised, which up to the present time seems to yield fairly satisfactory results.

About 150 grams of the sample is placed in a beaker and heated in a boiling water-bath untilentirely melted. The water is kept boiling for at least one hour and is then allowed to cool gradually without removing the beaker from the bath until the temperature is reduced to about 75°–80° F. It is then allowed to stand for at least twelve hours in a moderately warm place.

In practice the beaker immersed in the warm water of the bath is left standing in the laboratory over night at the ordinary room temperature which is usually all that is necessary excepting in very warm weather when the temperature should be reduced by artificial cooling.

This process causes the solid fat to crystallize, which being accomplished, fifty grams of the sample is weighed from the beaker after its contents have been thoroughly mixed by means of a glass rod or spatula, and is carefully wrapped in a double thickness of Canton flannel in which it is subjected to pressure in a small screw press.

The pressure should be applied very gradually, especially at first, and should be continued until the screw has been forced down as tightly as possible. After standing a few minutes to permit the oil to drain off, the contents of the press are removed and the cake of solid fat, consisting essentially of stearin, is easily separated from the cloth in which it is wrapped and can then be weighed.

The press used is called "Osborne's Patent Beef Press," and can be obtained in almost any hardware store, and is used for domestic purposes, such as the preparation of "beef tea," etc.

The length of time required is usually at least one hour, and the temperature seems to be a matter of comparative indifference provided, of course, extremes are avoided.

No great accuracy is claimed for this method, and that it is based on any thing like *strictly* scientific principles remains to

be proved, but the following results will, I think, show that it is what it is claimed to be, *i. e.*, a useful, if rough method for the assay of these manufactured compounds, and it is especially valuable as a preliminary operation in the more extended process of analysis.

Mixtures of the various ingredients, *i. e.*, oleostearin, lard and refined cottonseed oil were made in the laboratory, of which the following, as well as many others, are typical examples :

No. 1.

	Grams.
Oleostearin	20
Lard	10
Cottonseed oil	70

No. 2.

Oleostearin	25
Lard	10
Cottonseed oil	65

No. 3.

Oleostearin	25
Cottonseed oil	75

No. 4.

Oleostearin	24
Lard	10
Cottonseed oil	66

which, when assayed by the above described method, yielded respectively :

Number.	Per cent.
1	19.6
2	25.2
3	25.8
4	25.2

The following are the results obtained with samples of different formulas submitted for analysis :

SAMPLE A.

	Per cent.
Oleostearin	30
Cottonseed oil	70

SAMPLE B.

Oleostearin	25
Lard	10
Cottonseed oil	65

SAMPLE C.

Oleostearin	25
Cottonseed oil	75

SAMPLE D.

Oleostearin	25
Lard	10
Cottonseed oil	75

SAMPLE E.

Oleosterian	25
Cottonseed oil	75

SAMPLE F.

Oleostearin	23
Lard	10
Cottonseed oil	67

SAMPLE G.

Oleostearin	23
Lard	10
Cottonseed oil	67

SAMPLE H.

Oleostearin	24
Lard	10
Cottonseed oil	68

SAMPLE I.

Oleostearin	25
Cottonseed oil	75

which, upon assay as above, gave the following percentages, respectively:

	Per cent.
A	29.2
B	26.4
C	24.4
D	26.2
E	25.2
F	24.6
G	23.9
H	24.4
I	24.5

All of the above assays would seem to show that the results yielded are correct to within about one and a half per cent., and in my opinion it would be perfectly safe to consider that as a reasonable margin of error.

In consideration, however, of the character of the process of

assay as well as the character of the mixture and of the samples analyzed, I do not believe the analyst would be justified in reporting any *exact* amount of oleostearin found and have therefore adopted the form of reporting that the sample submitted contained "not less than —— per cent., nor more than —— per cent.," the margin of the error being as stated.

UNITED STATES LABORATORY.

THE MEASUREMENT OF THE COLORS OF NATURAL WATERS.

BY ALLEN HAZEN.

Received January 30, 1896.

THE diffusion of more accurate information and more rational theories as to the causation of diseases during the past few years has resulted in simplifying and changing many of the problems presented in connection with the chemical analysis of public water supplies. The healthfulness of a water for such use is determined to a much greater extent than formerly, by critical inspections of the sources of supply, particularly in the case of surface waters; and information as to the size of the water shed, flow at different seasons, amount of storage and character of the storage reservoirs, together with full information in regard to the population on the water shed and the way it disposes of its sewage, are more important and frequently adequate in themselves to determine the wholesomeness or unwholesomeness of a water; and the use of chemical analysis in connection with the investigation of such problems is rather in serving as an index of the varying amounts of contamination at different times, than in showing the presence or absence of substances which are in themselves injurious to health. Bacterial examinations also, which have become so frequent and necessary in connection with analyses of this character, play also their part in measuring such fluctuations.

There are, however, several determinations which indicate in themselves substances desirable or undesirable in a public water supply, and among these perhaps the most important are the hardness, the color, and in the case of ground water supplies, the iron; and although the color is determined mainly for its own

sake, and because a colorless water is more desirable that a colored water, and not because of any direct relations that the results obtained may bear to the wholesomeness of the supply, the interest that attaches to the determination often makes it of no less importance than those of the ammonia or other organic constituents.

The importance of this question of color has long been felt, and numerous efforts have been made to devise means for measuring and recording the colors. The essential requirements of such a method are that the figures obtained for a given color shall be the same at all times and in all places, and that it shall be possible to reproduce the colors with certainty at any future time. It is also desirable that the figures obtained shall be as nearly as possible proportional to the actual apparent colors of the various waters, as seen under ordinary conditions.

Perhaps the simplest method of measuring the colors of waters consists in taking a solution with a color of substantially the same hue as the waters to be examined, and diluting it with various quantities of distilled water, producing a series of colors with which the waters may be compared and results of relative colors obtained. The most natural substance to use for the colored solution is a highly colored swamp water, but the results obtained with such a standard of color, although comparable among themselves, would hardly have further permanent value owing to uncertainty as to the color of the water used for comparison, and the certainty that this color would fade, and the impossibility of reproducing it with accuracy at a future time. It is evident that any such procedure cannot fairly be considered as establishing a standard of color, and that the colors must have some definite physical basis which can be formulated and described with certainty and which will allow them to be reproduced at pleasure.

Perhaps an ideal basis of description of color would be a statement of the changes in the numbers and intensities of the vibrations in white light produced by passing through a layer of the water under examination. These changes are, however, so hopelessly complex as to defy even the hope of ascertaining them, and even if they could be determined it is doubtful if a statement of them could be made simple enough to convey any

meaning to the ordinary mind as to the colors represented.

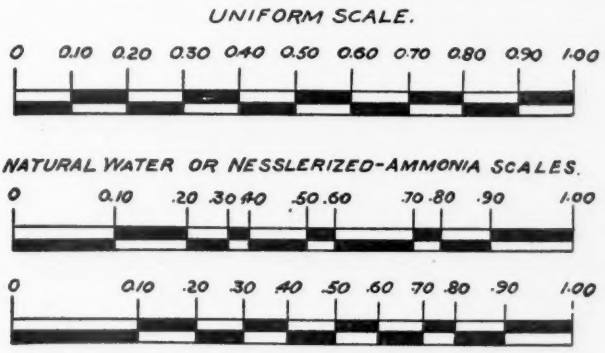
The most satisfactory standard which we can reasonably hope to realize is probably furnished by some other substance with a definite color, which can be produced at will, and which can be compared with the colors of waters, furnishing results of permanent value. One of the first attempts at such a standard was made by Messrs. Crooks, Odling, and the late Dr. Tidy,[1] who used solutions of ferric and copper salts in solution in independent vessels, which, superimposed upon each other, produced a color equivalent to that of the water. The fatal objection to this standard was that the color of the iron solution depends very largely upon the formation of basic compounds which vary in the intensity of their colors with very slight variations in acidity and with changes in temperature, so that the results obtained are open to a most objectionable uncertainty.

Another, and in some respects more satisfactory, attempt in establishing a standard was made by Prof. A. R. Leeds,[2] who suggested that extremely dilute solutions of ammonia after being nesslerized should be taken as the standards of color, the quantity of ammonia being taken as an index of the color produced. This standard was certainly most convenient, as the nesslerized ammonia standards are always present in laboratories for water analysis being required for another purpose, and it was believed that the colors had a sufficiently definite value to form a reliable standard.

This method has been widely used in the United States, and was employed by the author for several years and for the examination of some thousands of samples of water, until it became apparent that the variations and discrepancies in the results obtained were so great as to require serious consideration. As a result, a critical examination of the colors produced in this way was undertaken with the aid of my then assistant, Mr. Harry W. Clark, the results of which were published in full in the *American Chemical Journal*, **14**, 300. It was found in the course of the investigation that the colors produced depended not only upon the amount of ammonia used, but also upon a

[1] *Chem. News*, **43**, 174.
[2] *Proc. Am. Chem. Soc.*, **2**, 8.

whole series of conditions, many of which were not capable of exact control, so that the results obtained varied among themselves, even in the same laboratory at different times, to a most unsatisfactory extent. It was found that the colors produced depended not only upon the composition of the Nessler reagent and the quantity used, but even upon the way in which it was applied to the water containing the ammonia, and to a very



Irregularities in Nesslerized Ammonia and Natural Water Standards: From Report by Mr. FITZGERALD and Mr. FOSS in Report of BOSTON WATER BOARD for 1893.

large extent upon the temperature at which the experiment was made. It was further found that the colors produced were not at all proportional to the quantities of ammonia present, even under the most favorable conditions, owing in part to the very considerable color of the Nessler reagent itself, and in part to the fact that small amounts of ammonia produce less color relatively than larger quantities; and as a result of the combination of these two causes the colors increase in an irregular way that is most unsatisfactory. This irregularity of increase is well shown by a cut here reproduced from the report of Mr. FitzGer-

ald and Mr. Foss in the report of the Boston Water Board for 1893,[1] showing the colors of nesslerized ammonia and natural water standards received from the Institute of Technology when read against a single natural water standard in an ingenious colorimeter devised by the authors, and in addition the difference between the two lower scales shows how the standard differed at two different times.

The nesslerized ammonia standard has been improved in an important way by Mrs. Ellen H. Richards, of the Massachusetts Institute of Technology, who has for some years used standards of natural waters diluted with distilled water, as suggested above, and diluted to such an extent as to correspond with the nesslerized ammonia standards at a number of selected points, and with intermediate and lower standards prepared by interpolation between the selected points of comparison. This method of procedure eliminates to a certain extent the daily fluctuations in the values of the nesslerized ammonia standards, and also tends to smooth out the smaller irregularities in the scale, although the larger ones could hardly be removed without destroying the integrity of the scale itself. The method of procedure is, moreover, open to the more serious objections to the nesslerized ammonia standard in that the standards themselves depend for their original values upon the nesslerized ammonia standards of which the exact values are always open to question.

In a recent article published in the present volume of this Journal, page 68, by Ellen H. Richards and J. W. Ellms, an account is given of an attempt to establish in a more accurate and permanent manner the value of the standards used by comparing them with the Lovibond "Tintometer." This instrument consists essentially of a series of colored glasses which are superimposed upon each other to produce a color equivalent to that of a given sample of water or other substance. The tintometer in its construction and operation is so complicated as to render it impracticable, as Mrs. Richards states, to use it for the direct determination of colors in waters where many samples have to be examined, and its use is thus limited to determining

[1] *Franklin Institute*, 138, 91.

from time to time the values of the standards actually used for measuring the colors which would otherwise be subject to uncontrolled variations.

Several objections may be raised to the use of the Lovibond Tintometer as an ultimate standard of color. If we admit that the colors of the glass slips are permanent and will forever hold their color, we still depend upon the honesty and skill of the manufacturer of the instruments to produce glass slips of precisely the same values as those used in the original apparatus. It is of course conceivable that an apparatus should be continued in use with the same slips for many years, but eventually the slips would become worn or scratched and would require to be replaced, or the apparatus might be destroyed by fire or other accident; and in any case other laboratories buying new instruments will require to have new slips. It is thus seen that the values of the colors depend ultimately upon the honesty and skill of the manufacturer in preserving and reproducing an arbitrary standard, and not upon natural units.

It may be said as against this view that the values of the Lovibond units have been determined by comparison with the colors of solutions of definite chemical composition with such care and precision that it will be possible at future times to determine whether the slips then in use are really the equivalents of those now sold, and that it would even be possible to reproduce them in case the present standards were lost or destroyed. But against this statement it may be urged that it is much more rational, simpler, and better in every way to compare the waters directly with the chemical solutions which are the ultimate points of reference without the intervention of glass slips or other standards.

An attempt to do this was made by the author, who published[1] a description of a method of comparing the colors of waters with those of solutions of platinum and cobalt of known strength, the colors of which were absolutely definite and permanent, and capable of being reproduced with precision at any time, and not affected by temperature or other conditions likely to occur in well regulated laboratories. The method of stating the results

[1] *Am. Chem. J.*, 14, 300.

was a natural and simple one, namely, "that the color of a water is the amount of platinum, in parts per ten thousand which, in acid solution, with so much cobalt as will match the hue, produces an equal color in distilled water."

Since the publication of this article the platinum standard has been used in laboratories under my direction, and by my successors, and in other and independent laboratories for the measurement of colors in many thousands of samples of water, and with such uniformly satisfactory results[1] that I believe it only fair to say a word in regard to the objections raised to the standard by Mrs. Richards in the above mentioned article.

The first of these objections is that there is an excess of orange to yellow in the standard, which, if I understand the language correctly, means that the standard is redder than the waters to be examined. This contingency was provided for in the original article by making the platinum the standard of color and allowing the cobalt to be varied as required to match the hues of the waters. The quantity of cobalt in proportion to the platinum which I suggested, namely, one-half as much metallic cobalt as platinum, was the result of my experience of thousands of samples of water prior to the publication of that article, but as waters from different sources vary in their hues, it was fully recognized that it might be desirable in other cases to use a different proportion of cobalt from that suggested; and if it is found that the quantity of cobalt suggested produces a standard too red for a given set of waters, it is only necessary to make a fresh standard with a somewhat smaller quantity of cobalt to be determined by experiment, when it will be found that the hue matches the waters as closely as it is possible for any single standard to do.

As a matter of fact, standards containing a quarter less and others containing a quarter more cobalt than the amount suggested have been repeatedly used by the author and by others for special purposes, and, while the hues of some waters are more accurately matched, the results as a whole have hardly warranted any change in the proportion suggested for ordinary practical work.

[1] Report of Boston Water Board, 1893, p. 85. Report of Massachusetts State Board of Health on Metropolitan Water Supply, 1895, p. 177. *J. Franklin Institute*, **138**, 403.

The second objection is that the standard is not suitable for the measurement of the deeper colors. This is indeed an important question, and had been thoroughly canvassed by the author and his assistants before the publication of the process, and the means for avoiding difficulties from this source were distinctly stated in the article, although the reasons for the precautions to be taken were not perhaps stated as fully as was desirable.

One of the first facts to be learned by persons studying the colors of solutions is that solutions having the same color in one depth or dilution are not necessarily of the same color in greater or less depths or dilutions. The truth of this statement was most strikingly shown in an article published by the author, in connection with Mr. Harry W. Clark[1] in connection with the colors of the various nitrophenols in various dilutions, in which it was shown, for example, that alkaline solutions of ortho- and paranitrophenols are of about the same color when solutions containing one-tenth or a part in a million of nitrogen are seen in depths of 200 mm., while with more dilute solutions the para is more highly colored, and with more concentrated solutions the ortho has the deeper color, and the variations are so astonishingly great that with the most concentrated solutions examined the ortho produced as much color as more than thirty times its weight of paranitrophenol.

The explanation of this remarkable phenomonon has been clearly given by Mr. Desmond FitzGerald and Mr. William E. Foss, in the annual report of the Boston Water Department for 1893.[2] It is there stated that the amount of light which passes through successive equal layers of an absorbing solution diminishes in geometrical progression as the number of layers increases in arithmetical progression ; and as the coefficient of transmission varies with different solutions, it often happens that a water matches the standard very closely in hue in a short depth, but appears of quite a different hue in a greater depth. That is to say, taking an extreme case, the coloring-matter in one solution, owing to its chemical or physical properties, absorbs a large percentage of the light from a narrow band of the spectrum,

[1] *J. Anal. Appl. Chem.*, 5, 301.
[2] *J. Franklin Institute*, 138, 401.

while another substance to produce the same apparent color absorbs a small percentage of the light from a broad band in the spectrum. In the first case as the solution is increased in depth or concentration, its color at first rapidly increases until all or nearly all of the rays of light which it is capable of absorbing are exhausted, and further increase in depth effects but little further change in color. In the second case, owing to the smaller percentage absorption of the light rays the color increases to a much higher limit, and in great depths the solution has a much deeper color than is possible in the former case where the action is confined to a narrow band in the spectrum.

A combination of absorption bands having different relative absorptions in the same solution gives rise to the change in hue so often noticed with changing depth or dilution. Thus it is a matter of common experience that a water which is a pure yellow or even greenish when seen in slight depth becomes orange and even quite red when seen in great depths. The way in which these differences occur was well shown by a diagram, in the report mentioned, showing how the standard matching the water at low depth, constantly diverges from it as the depth increases.

There are two possible means of remedying this evil. The first would be to secure a standard in which the coloring-matter was identical in composition with the coloring-matter in the natural waters. Such a standard could obviously be only the natural water standard which, as shown above, is really no standard, but only a go-between between the waters and the real standards. The other method of avoiding the difficulty is to make comparisons only in such deqths that the divergencies between the standards and the waters will not be considerable.

As stated in the report quoted above, the quantity of light transmitted decreases in geometrical progression as the depth increases in arithmetical progression. Let us say that the first cm. of water intercepts one per cent. of those rays of light, whose interception produces the effect of color in the water. The second cm. of water will then intercept one per cent. of the remaining rays, or 0.99 per cent., and the third cm. will intercept one per cent. of the 98.01 per cent. reaching it, or substan-

tially 0.98 per cent., leaving 97.03 per cent. As the color produced is measured by the difference between the light remaining and the full light, we may express the colors produced by one, two, and three cm. of water as, respectively, 1, 1.99, and 2.97. These figures are obviously substantially proportional to the depths; the error of one per cent. in the last case being entirely too small to be taken into consideration. If, however, the process is carried further, the error increases as rapidly as the square of the depth, and at no very remote point becomes important and serious. As an illustration of the substantial correctness of this proposition, the above-mentioned ortho- and paranitrophenols may be mentioned. Notwithstanding the most extraordinary differences between the colors of the comparatively concentrated solutions of these substances, the colors produced by extremely dilute solutions are substantially proportional to the amounts of the respective substances present, and so long as certain limits are not passed, their colors increase at the same rate with increasing depth. The differences between these substances at various dilutions are, however, vastly greater than those between the platinum-cobalt standard and natural waters, and the differences in the latter case with increasing amounts of color are no greater than would be sure to be found with almost any two coloring-matters not of the same chemical composition.

The point to which it is safe to carry the reading of colors is determined by practical experiment and not by theoretical considerations. It was stated by the author in the original paper that up to a point corresponding to colors of 0.9 in a depth of 200 mm., or corresponding lighter or deeper colors in greater or less depths, the variations between the hues of the platinum standard and actual waters were so slight as to be unimportant. In Mr. FitzGerald's report mentioned above, it is stated that colors up to a depth of 1.0 for the same depth can be satisfactorily compared with the platinum standard, this limit being ten per cent. above that suggested by the author, and as long as colors are not measured above these depths the errors introduced are entirely unimportant; and while it is recognized that serious errors might be introduced by the attempt to read much deeper colors, this contingency was distinctly provided against by stat-

ing that all waters with deeper colors should be read in a less depth of liquid, or what is practically more convenient, and as far as I have been able to ascertain, equally accurate, the water should be diluted with one, two or more times its volume of distilled water, the color of the diluted water read and multiplied by a proper factor. Mrs. Richards finds it necessary to adopt this same procedure, even with the natural water standards, because, as a matter of fact, the coloring-matters in different waters vary from each other, and the hues produced in different depths also vary in the same way as the hue of the platinum standard varies from that of a water, only in a less degree, and with the natural water standards it is only possible to read accurately colors as high as 2.0, or only twice as high as the limit with the platinum standard.

This dilution of waters with high colors may be objected to on the ground that, a water having, for example, a color of 2.0 does not in reality contain twice as much coloring-matter as a water with a color of 1.0, and that correct results will not be obtained in this way. This is, in fact, the case with the nesslerized ammonia standards and with the natural water standards based upon them, as was shown by the author, who stated that with these standards "color 0.5 is only twice as deep as color 0.2; color 0.8 is only twice as deep as color 0.3; color 1.0 is only twice as deep as color 0.4, etc.;[1] and this very fact is one of the serious objections to the use of these standards. With the platinum standards, on the other hand, the numbers expressing the colors, as nearly as can be determined, are proportional at every point to the actual coloring-matters present, and this simple relation is one of the important practical advantages of the standard.

As a matter of fact, a great majority of the waters, even from swampy regions, have colors low enough to allow accurate direct readings with the platinum standard, and the necessity of diluting the more deeply colored waters occasionally found cannot be regarded as a practical objection to the process. In actual use the convenience of operation, the simplicity of the apparatus required, the accuracy of the work obtained even with unskilled

[1] *Am. Chem. J.*, 14, 308.

operators, and the permanency of the standard, even under exceptionally unfavorable conditions, which has far exceeded anything for which we dared to hope when the standard was first used, have abundantly demonstrated its utility; and in view of the ease and accuracy with which it is possible to compare directly the colors of natural waters with metallic solutions, which are, in fact, the only reliable ultimate standards now in use or known, it seems most unfortunate and in every way undesirable to introduce arbitrary go-betweens, not having definite values of their own or capable of being reproduced or controlled except by comparison with other standards.

TECHNICAL ANALYSIS OF ASPHALTUM. No. 2.[1]

By Laura A. Linton.

Received January 3, 1896.

MY former article[2] on this subject has been so favorably received and commented upon that I have been encouraged to offer a second contribution with the object of adding a few more facts to the literature of the subject, as well as to point out certain changes in the method of analysis outlined in the first article, which changes have been suggested by recent analytical work.

The method universally employed for the determination of the incorporated water of asphaltum is that of estimating the loss in weight of the substance when exposed to a temperature of 100° C. The possibility of a loss of more or less of the inherent volatile matter when heated to such a high temperature must have occurred to every one engaged in the analysis of asphaltum. A series of experiments made during the past few months has confirmed my suspicion that such is the case.

The experiment proper consisted in heating a weighed portion of asphaltum in a combustion tube, the general arrangement of the apparatus being the same as that employed in the determination of water in organic analysis. The temperature was gradually raised from the temperature of the room to that of boiling water. The tube was swept out before and after heating with either dried air or dried hydrogen. Simultaneously with

[1] Read at the Cleveland meeting, December 31, 1895.

[2] This Journal, 16, 809.

this experiment two other weighed portions of the same asphaltum were dried, one in an oven at 100° C. to serve as a check upon that portion dried in the combustion tube, while the other portion was dried in the sun.

As the method of sun drying requires several days it was done in a room as free as possible from dust and, to increase the temperature and at the same time to exclude all foreign matter, the samples were placed in large watch glasses with watch-glass covers fitting loosely to allow of circulation of air. In this lens-like arrangement the maximum temperature did not exceed 50° C. On cloudy days the drying was necessarily done in the oven below 50° C.

These experiments showed that the asphaltum tested did not oxidize below 100° C., as aspiration with dried air and dried hydrogen gave the same results; and also that all moisture is driven off below 50° C. while between 50° C. and 100° C., a certain portion of oily matter is lost, this oil invariably collecting in drops about the mouth of the combustion tube. In the light of these facts it becomes clear that the old method of determining moisture, if it is to be determined at all, is incorrect since the percentage lost on heating the asphaltum to 100° C. includes not only the water but also that part of the petrolene volatile below 100° C.

The moisture associated with an asphaltum being hygroscopic, as in evident from the fact that the same specimen carries a constantly varying proportion depending on atmospheric conditions, it should never be estimated as a constituent part of the asphaltum, particularly in making analyses for purposes of comparison.

In making all of my recent analyses, as a preliminary, I have air dried to a constant weight several grams of the sample to be analyzed before weighing out the portion to be treated with the different solvents, thus entirely excluding water from the percentage composition of the asphaltum.

A second departure from the method previously given is a purely mechanical one. As a matter of convenience I have discarded the use of the Erlenmeyer flask, the substance being weighed out on balanced filter-papers instead. In this way all digestion is done in separatory funnel. This method of treat-

ment is very simple and the results obtained are good, but care must be taken that the solution in the funnels does not become too concentrated before running off through the tap, otherwise the petrolene precipitates itself, more or less of it adhering to the outside of the filter-paper. To prevent this the petroleum either may be drawn off every few minutes until the greater part of the petrolene has been extracted after which it is perfectly safe to allow the digestion to continue for hours in removing the final traces.

Lastly, I have obtained some interesting and, in my opinion, important results by fractionating the asphaltene, determining it in two portions ; that soluble in boiling turpentine and that soluble only in chloroform. The process is a very tedious one on account of the difficulty of removing the very last trace soluble in boiling turpentine, but the results that follow are a sufficient warrant for the expenditure of so much time, which, for the specimens analyzed, ranged from one to four weeks. In order to secure concordant results in duplicate analyses I found it necessary to pursue the following course :

After the removal of the petrolene the residue on the filter was digested in boiling turpentine until the filtrate was colorless, when the contents of the filter were washed in alcohol and dried at 100° C. If, on drying, a black, semi-liquid substance separated from the mass, this was an indication that the turpentine fraction had not been entirely removed, in which case the process was repeated. In the most refractory specimens this treatment was applied many times. The tardy yielding to the solvent power of the turpentine is doubtless largely due to the fact that the turpentine does not readily penetrate the mass and it may be, also, that the chloroform fraction prevents the action of the turpentine just as gold protects silver from the action of nitric acid. The completion of the process is always indicated by the appearance of the dried residue which, after the complete removal of the turpentine fraction, is invariable a loose, brown powder without coherence. This treatment shows that part of the asphaltene soluble in boiling turpentine to be a black, viscous, semi-liquid substance resembling tar and having a melting point at or below 100° C.

Another fact, which may prove valuable as well as interesting, is clearly brought out in this fractionation of asphaltene and that is that not only do the "aged" varieties of asphaltum contain a larger petcentage of asphaltene but the turpentine fraction becomes a smaller proportion of the total bitumen while the chloroform fraction becomes larger.

An investigation of the table of the percentage composition of the following varieties of asphaltum will confirm this statement:

No. 1. An average sample of land asphaltum from the island of Trindad.

No. 2. Altered or "aged" (iron pitch) Trinidad land asphaltum.

No. 3. Altered or "aged" Trinidad land asphaltum.

No. 4. An average sample of Trinidad lake asphaltum.

No. 5. An altered or "aged" Trinidad lake asphaltum.

No. 6. An altered or "aged" Trinidad lake asphaltum.

No. 7. An altered or "aged" (iron pitch) Trinidad lake asphaltum.

No. 8. Asphaltum from Montague Co., Texas.

No. 9. Turrellite from Uvalde Co., Texas.

No. 10. Asphaltum from near Ardmore, Indian Ter.

No. 11. Grahamite from Ritchie Co., W. Va.

No. 12. Scyssel asphaltic rock from Eastern France.

Sample.	Petrolene.	Turpentine fraction.	Chloroform fraction.	Asphaltene.	Total bitumen.	Ratio of chloroform fraction to total bitumen.	Organic matter not bitumen.	Mineral matter.
1	33.73	15.67	3.179	18.849	52.579	1 : 16	11.528	35.886
2	33.574	13.7	9.627	23.327	56.901	1 : 6	8.414	34.684
3	21.362	15.2	15.112	30.312	51.674	1 : 3	9.85	38.375
4	35.40	12.300	5.287	17.587	52.987	1 : 10	10.962	36.100
5	26.925	18.613	6.687	25.3	52.225	1 : 8	11.237	36.537
6	19.25	22.35	10.962	33.312	52.562	1 : 5	9.562	37.875
7	22.25	9.785	12.54	22.325	44.575	1 : 4	8.937	46.462
8	7.538	1.601	trace	1.601	9.139	....	....	90.861
9	8.786	3.267	trace	3.267	12.053	....	....	87.947
10	9.503	0.9905	trace	0.9905	10.4935	....	....	89.5065
11	49.959	17.458	32.583	50.041	100.00	1 : 3	....	....
12	7.486	3.945	0.371	4.316	11.802	1 : 31	....	88.198

I am not yet prepared to say that the turpentine fractionation of asphaltene, if made in the case of the asphaltum obtainable from

different parts of the world would indicate the relative "ageing" of the different varieties, but my experience with Trinidad Pitch inclines me to think that this will prove the case when such analyses are made. However, even if the turpentine determination should prove of no value as indicative of "ageing" processes in asphaltum, there is still a weighty reason why it should not be abandoned.

The marked physical difference between the turpentine and chloroform fractions would seem to indicate the probability of a chemical difference and I am sure that when an ultimate analysis of asphaltum has been made, as it will be in the near future, that turpentine as a solvent will be proven to have its place.

I am aware that some object to the use of turpentine because it is not pleasant to work with, particularly when it is boiling hot, but in scientific research we are seeking truth and not our own pleasure and convenience. If the cooperation of chemists engaged in the investigation of asphaltum could but be secured the solution of the problem would be a speedy one. But this may not be, so solvents are accepted or rejected at will with apparently no principle ruling in the choice. One chemist of wide reputation rejects chloroform and uses carbon disulphide as the final solvent in the extraction of bituminous matter.

I have analyzed many different varieties of American and foreign asphaltum and, with the exception of the Neufchatel, which is practically all petrolene, and the asphaltum from Texas and Indian Territory, all yielded more or less bituminous matter on treatment with chloroform after exhaustion with other solvents. Now, because the Neufchatel and a few other varieties need no chloroform for the extraction of bitumen, shall this solvent be stricken from our category? rather let our scheme be so broadened as to be applicable to every variety of asphaltum the earth holds.

UNIVERSITY OF MICHIGAN.

DISCUSSION.

A. H. Sabin: This asphaltum business is one of a great deal of commercial importance. There are a great many things about it that we do not know; I hope somebody here can tell us a few things.

In the first place asphalts are a very peculiar set of bodies. The most attention has been given of late years to Trinidad, because it has been used for paving purposes, and has been of immense commercial importance. It has generally been overlooked by the chemists who have worked on this line, that compartively recently the commercial introduction of asphalts from other sources has been of great importance. Ordinarily chemists analyze either the Trinidad or Egyptian asphalts. The Egyptian asphalt is considered to be a representative of the high grade asphalts which are to be found in the East, while the Trinidad asphalt is a cheaper variety, very elastic, and contains a large amount of foreign matter. Commercially, as a matter of fact, the Egyptian asphalt is higher priced than the American, and so are all the Eastern asphalts. The fact has been known for a number of years that large deposits of asphalt are found in Utah and Colorado known as Gilsonite and Uintahite. These have been put on the market at such low prices that in St. Louis, I understand, Gilsonite is used in the paving trade. Gilsonite is an exceedingly pure asphalt. It is a very interesting substance, and it is hoped that future investigations will take into consideration the fact that these more recently discovered beds, which promise to be of more commercial importance than the Trinidad deposits, are practically inexhaustable. Some asphalt deposits are being developed in South America. We have the general statement made in Dana's Mineralogy, which so far as I can learn is based upon the well known investigations made long ago in France, and partly on some work chiefly in the line of checking results, which was done in the Sheffield Scientific School, that all petroleums contain more or less asphalt in solution, and that it is generally believed that asphalts are a sort of petroleum residue, and that the naturaral asphalts differ from the asphalts which are obtained as petroleum residues in being oxidized compounds. As near as I can find out that term "oxidized" is merely a conventional term. It means that the hydrogen has been removed, not that the oxygen has been added, although they show upon analysis that some oxygen is present. The chief difference apparently is that compounds containing hydrogen have escaped. The differ-

ence between hard and soft asphalts is just that difference that the mineral oils have been removed in some way or other from the asphalts and they are therefore hard; whereas some of them like the Trinidad have a considerable amount of mineral oily matter in them and are very elastic and well adapted to paving purposes. The presence of these ingredients, while it adds to their durability, detracts from their usefulness for other technical purposes, because mineral oil is comparatively easily removed by the action of the weather, while the hard asphalts not containing this volatile and soluble matter can be made elastic by being compounded with linseed oil and other substances, and in that way can be made immensely more permanent than elastic asphalts. This is inapplicable to paving, but it has large application. There is a good deal of commercial asphalt on the market under the name of Maltha, which was used as long ago as the time of Rliny. The name has been recently applied to asphalt from southern California. It is obtained in various degrees of hardness from a thick liquid to a solid, and is a good illustration of the so-called artificial asphalts. Of course, it is a natural product. Nothing has been done to it except the volatile portions have been distilled out of it. I should like to know whether these asphaltic constituents are present in all petroleums, or whether they are in some cases or in all cases produced by the action of high temperature upon the crude oil, and whether these differ from natural asphalt in oxidation or in what way?

Prof. Mabery: I have had some experience with asphalts in the way of observation, and to a certain extent experimentally. At Oil Springs, in Canada, a surface oil is found that is very heavy, with a specific gravity of 90, and in the vicinity of beds of asphaltic pitch. There is no question that there has been a change through the heavy surface oil into the asphalt. Some constituents of petroleum are very unstable; for example, at a temperature of 80°, *in vacuo*, a distillate was collected, which, after standing two years and then again distilled, decomposed into tar which could not be distilled without carbonization, doubtless the result of polymerization.

In regard to the origin of petroleum there is a great deal of

conjecture. So far as oxidation is concerned, the amount of oxygen contained in it is small. Recently we examined a product made from petroleum residue which resembles in some respects natural asphalt. It may be that some of you have heard of it under the name of Byerlyte. It is manufactured in this city. The process consists in taking the heavy oil after the burning oil is distilled, putting it into the still, passing in currents of air and applying a gentle heat to the bottom of the still during five or six days. Then the product is drawn off. It contains no fixed carbon. It resembles in some respects natural Gilsonite. So far as practical uses are concerned they are closely related. With reference to oxidation the quantity of oxygen does not appear to be very different from that in crude oil. As Mr. Sabin suggests, we cannot look upon oxidation in the production of asphalt as the introduction of oxygen, but rather as the removal of hydrogen, and that is doubtless related to certain features of polymerization. It seems to be a conversion of the unstable hydrocarbons into higher products. Concerning the composition of these products we know very little.

Other products have come under my observation which are on the market at the present time and used for insulators.

In some heavier sludges polymerization takes place when substances are formed closely resembling asphalt. There is a great field of investigation surrounding asphalt, but it is an exceedingly difficult subject.

The determination of water is an interesting question. It is practically impossible to remove water from petroleum by the ordinary methods. Ohio and Canada petroleum may stand for months, and when it is again distilled, water will appear to a considerable extent. Those pure hydrocarbons, which I showed last evening, can not be dried with calcium chloride. We found the moisture could only be removed by sodium, and after it is removed, upon exposure to the air, it reabsorbs moisture with great rapidity. Probably the same thing would apply to asphalt. Of course, in heating, the water will be removed, but if the products are again exposed to the air they will reabsorb the water. This question should be undertaken from the standpoint of thorough chemical investigation.

Mr. Sabin: These artificial asphalts have some very remarkable commercial differences from the natural asphalts. For example, they resist the action of sodium hydroxide. Sodium hydroxide seems to combine with almost all natural asphalts, but not with pitches or tars. In the same way for the purpose for which I use it, it is impossible to use it as asphalt, or in the way in which you can use any natural asphalt. You can not melt it alone without decomposition. It can be melted with other substances, such as rosin or some mineral oils. But it does not mix with the vegetable oils, such as linseed by itself. It is used very successfully as an insulator, as many of the pitches are. It has many useful and valuable qualities, which none of the asphalts have, especially that of resisting caustic alkali, but for many purposes it differs as widely from natural asphalt as if it were entirely and absolutely a different substance.

REVIEWS.

THE VALENCY OF OXYGEN AND THE STRUCTURE OF COMPOUNDS CONTAINING IT.

Hydrogen Dioxide.—In a recent issue of the Berichte der deutschen chemischen Gesellschaft[1] J. W. Brühl calls attention to the significance of recent work of Moritz Traube upon the structural formula of hydrogen peroxide. Traube found that when, in the electrolysis of water, the electrodes are separated by a diaphragm, no hydrogen peroxide forms. If now air be blown through the solution in contact with the cathode, hydrogen peroxide forms in quantity, presumably by the oxidation of the nascent hydrogen by the molecular oxygen of the air. Traube has also shown that when silver oxide is reduced to metal with formation of water and free oxygen, the latter comes from the peroxide, the oxygen of the water coming from the silver oxide, thus:

$$Ag_2O + H_2O_2 = Ag_2 + H_2O + O_2.$$

The constitutional symbol of hydrogen peroxide is usually written H.O.O.H. If this be correct we should expect it to unite with the olefines forming glycols by direct addition. Glycols seem not to be formed in this way, except in the case of

[1] 28, 2847.

ethylene glycol, which, according to Carius,[1] is formed by adding ethylene to hydrogen peroxide in "verhältnissmässig sehr kleine Mengen." But even if this reaction takes place it would not prove the correctness of the above structural formula since glycols are formed by acting on the olefines with potassium permanganate. The formation of hydroxides by the action of hydrogen peroxide on the metals, such as zinc, is inconclusive for the same reason.

Neither does the formation of salts, such as barium dioxide from hydrogen peroxide prove anything, since we know many acids which contain no hydroxyl.

Because of the fact that in all its decompositions, molecular and not atomic oxygen, was liberated, and of its formotion from molecular oxygen and atomic hydrogen, Traube wrote the symbol:

H.O:O.H.

Additional interest attaches to this question since Wolffenstein has shown[2] that hydrogen peroxide may be concentrated and obtained by distillation in a vacuum as an explosive, nearly anhydrous substance.

Spring has recently shown[3] that thick layers of hydrogen peroxide have a bluer color than water, and since ammonium iodide is colorless, and NH_4I_3 and NH_4I_4 are green or violet. this indicates the possible presence also of molecular oxygen in the peroxide.

From his determination of its specific heat Spring concludes that the elements H_2 and O_2 in combining have used only a part of their potential energy, which is more nearly in harmony with Traube's formula than with that commonly accepted.

Brühl has now[4] determined the index of refraction of the pure nearly anhydrous substance and the specific gravity, and from these he has calculated the specific refraction and dispersion and the molecular refraction and dispersion. The molecular refraction and dispersion is found to be:

$$M_a = 5.791.$$
$$M_{Na} = 5.817.$$
$$M_\gamma - M_a = 0.136.$$

If we subtracted from the corresponding constants for water, the constants for the hydrogen atom, the values for the latter being nearly the same as in its compounds, we get the following:

[1] *Ann. Chem.* (Liebig), **126**, 209.
[2] *Ber. d. chem. Ges.*, **27**, 3307.
[3] *Ztschr. anorg. Chem.*, **8**, 424; **9**, 205.
[4] *Loc. cit.*

	M_a.	M_{Na}.	$M_\gamma - M_a$.
HOH	3.69	3.71	0.09
H	1.10	1.05	0.04
HO	2.59	2.66	0.05

This would give, doubling these values for hydrogen peroxide:

	M_a.	M_{Na}.	$M_\gamma - M_a$.
H.O.O.H	5.18	5.32	0.10

These values are, however, much smaller than those observed for hydrogen peroxide, (see above). The easiest explanation of the fact that the spectrometer constants of hydrogen peroxide are considerably larger than would correspond to the symbol H.O.O.H, lies in the assumption of multiple union between the oxygen atoms. This would necessitate the assumption of multiple union in ordinary oxygen, and while this is not proven, it is indicated by the recent work of Olszewski and Witowski,[1] and especially by the work of Liveing and Dewar[2] on liquid oxygen. If we compare the optical equivalents of two atoms of oxygen in water with the constants of molecular oxygen, we get:

		M_a.	M_{Na}.	$M_a - M_\gamma$.
2O in water		2.968	3.212	0.036
O_2 as molecular oxygen	liquid	3.958	3.964	0.069
	gaseous	....	4.09	....

This shows that the optical constants of the molecular oxygen are considerably greater and the dispersion double that of the oxygen in water. This is, however, the best criterion of multiple union of the atoms.

But if in hydrogen peroxide the oxygen atoms are united by multiple union, fewer valencies must be concerned than in molecular union.

If this conjecture be granted, we should find the oxygen constants from hydrogen peroxide somewhat smaller than the molecular oxygen, and this is the case, as is seen below:

		M_a.	M_{Na}.	$M_\gamma - M_a$.
Oxygen in water (2O)		2.968	3.212	0.036
Oxygen, O_2, in hydrogen peroxide		3.591	3.717	0.055
Oxygen, O_2, molecular	liquid	3.958	3.964	0.069
	gaseous	....	4.09	....

If we assume Traube's symbol for hydrogen peroxide to be correct, we must call oxygen trivalent, for which we have no

[1] Bulletin Acad. Cracovie, Oct. *1897*, 341.
[2] Phil. Mag., 37, 268.

warrant; neither is any member of the oxygen group of the periodic system known with a valence of three.

On the contrary, sulphur, selenium and tellurium are bivalent and quadrivalent, and several compounds indicate the quadrivalence of oxygen, such as Rose's quadrantoxides, (Ag_4O), but especially the compound of Friedel[1] $HCl(CH_3)_2O$. If it be granted that oxygen may be quadrivalent, we may then write hydrogen peroxide:

H.O:O.H.

All the known properties of hydrogen peroxide; its formation from nascent nydrogen and molecular oxygen; its decomposition by nascent oxygen; its endothermic decomposition are explained by this structural formula.

Constitution of Ozone.—On the assumption of the quadrivalence of oxygen, the symbol of ozone may be either

No data are yet at hand sufficient to decide this question.

Constitution of Carbon Monoxide.—For many years carbon monoxide has remained as the single illustration of the bivalence of carbon. If we assume that oxygen is quadrivalent, however, this difficulty at once disappears. The spectrometric behavior of carbon monoxide favors this view. Brühl has shown[2] that carbon monoxide has the following molecular refraction:

	$M_{Na.}$
Found	5.04
Calculated for C:O	4.79

This small difference is, however, many times greater than the possible experimental error.

The assumption of the structure C:O for carbon monoxide involves the assumption of unsaturated oxygen in numerous carbon compounds; at least in those containing an uneven number of carbon atoms; but we have also many sulphur and nitrogen compounds in which these atoms are bivalent and trivalent respectively.

The Constitution of Water.—In another paper Brühl considers[3] the result of this new view upon the constitution of water. It is known that in aqueous solutions of salts of strong acids and bases, the observed alteration of the freezing-and boiling-points is nearly double the normal amount deduced from van't Hoff's

1 *Bull. soc. Chim.*, **24**, 160, 241.
2 *Ber. d. chem. Ges.*, **24**, 663.
3 *Ber. d. chem. Ges.*, **28**, 2866.

equation. We know also that Arrhenius has accounted for this by supposing that in such solutions the salts are decomposed into their ions.

It is known, further, that many organic substances, such as the fatty acids, oximes, alcohols, etc., form double molecules or molecular complexes when dissolved in hydrocarbons, chloroform and carbon disulphide, and that these complexes are broken up when these substances are dissolved in water, and to a certain extent also when dissolved in alcohols, ethers, esters, ketones and phenols. The latter class of solvents are to a certain extent also ionizing, since when saturated with hydrochloric acid they act as conductors, while solutions of hydrochloric acid in benzene and other hydrocarbons are non-conductors.

Why water so far surpasses other solvents in its power to allow of this dissociation is not known, but the explanation is easily found if we write water as an unsaturated compound giving oxygen four bonds, thus:

$$H \cdot \dot{\underset{\cdot}{O}} \cdot H.$$

In fact the properties of water indicate almost with certainty that it is unsaturated, for nearly all substances have a tendency to unite with it—are hygroscopic. Numerous hydrates and compounds with water of crystallization exist, and, finally, water is the universal solvent. The supplementary valencies of the quadrivalent oxygen are evidently the cause of the formation of the ions, and the molecular aggregates the reason of the dissociating power of the water.

This notion receives further support when we remember that all those organic solvents which are known as good dissociation media contain oxygen—ethers, alcohols, esters, ketones, phenols, urethanes, etc.—while those free from oxygen, such as the hydrocarbons, chloroform, carbon disulphide, carbon tetrachloride have little or no power to cause dissociation.

EDWARD HART.

THE HISTORY OF ELECTRIC HEATING APPLIED TO METALLURGY.[1]

Sir Humphry Davy is justly regarded as the father of dry electro-metallurgy. After making full allowance for the unusual facilities at his command, it still remains that his intelligent, faithful and extended use of his facilities is worthy of the utmost honor.

[1] Read before the Washington Section, Dec. 12, 1895.

It often happens, however, with epoch-making events that a close search reveals previous indications, so in this case it is found that not only was Davy's dry work preceded by a course of wet electro-chemical experiments, as pointed out by Davy himself, but also an important contribution to dry electro-metallurgy had been made long previous to Davy, and that this even preceded the first observed decomposition of water by the current.

In 1795 a Dutch book of 396 pages was published at Haarlem by Martinus Van Marum, entitled "Second Continuation of Experiments by Means of the Teyler Electric Machine."

I have not seen the original book, but various notices[1] of it appeared in the Journals at the time. From these it appears that Van Marum was a thoughtful and exhaustive investigator. His investigations took a wide range and included much outside our title. He, however, not only observed the heat produced by the passage of the current, but he actually measured it. In one instance the temperature of his apparatus, designed for measuring this effect, rose from 61° to 88° in three minutes, and to 112° in five minutes. He volatilized phosphorus in a tube and proved it to be "phosphor gas." He investigated the suitability of metals for lightning rods and determined that copper was twice as good as iron. He oxidized metals by the current and performed various melting experiments. He had a scale to measure the current and at twenty-four 100 feet of iron wire, $\frac{1}{240}$ inch in diameter, melted, while 104 feet melted and separated into globules. He also melted longer pieces, but concluded that such melting tests were not worth the while. Sixty feet of No. 11 wire, $\frac{1}{150}$ in diameter, melted at 24.5, but at the same point thirty-six feet of No. 1 wire glowed its full length, one-half being quite blue and the rest slightly oxidized. Quartz was split up and slightly melted.

Having oxidized the metals by the current, he conceived the idea that the oxides could be again reduced to the metallic state by the application of larger amounts of the current. It does not appear that he actually used electrically produced oxides to test this idea, for he not only did test it, but also actually collected and tested the gas given off.

His furnace, if I may so call it, was a glass tube with platinum electrodes. In this he put his oxide and passed the current with the following results: Red lead gave lead on the surface of the tube in a few moments that could be gathered up, and in twenty minutes he collected three-quarters cubic inch of gas. White lead gave lead in smaller amounts. Tin oxide gave no metal.

[1] *Aeltern J. der Physik.*, **4**, 1; **6**, 37, 360; *Neue J. der Physik.*, **3**, 1: *Pog.*, **1**, 68, *et al.*

Red oxide of iron gave no metal. Red oxide of mercury gave mercury and a little gas. He proved that the gas given off was oxygen and credits the decomposition to heat.

In a lecture delivered during the latter part of his life, Sir Humphry Davy gave a history of electro-chemistry, from which I take the following statements:

"The true origin of all that has been done in electro-chemical science was the accidental discovery of MM. Nicholson and Carlislie, of the decomposition of water by the pile of Volta, April 30th, 1800." "In the month of September, in the same year, I published my first paper on the subject of galvanic electricity in Nicholson's Journal, which was followed by six others, the last of which appeared in January, 1801. In these papers I showed that oxygen and hydrogen were evolved from separate portions of water, though vegetable and even animal substances intervened, and conceiving that all decomposition might be polar."

"In 1804, MM. Heisenger and Berzelius stated that neutro-saline solutions were decomposed by electricity, and the acid matter separated at the positive, and the alkaline matter at the negative poles; and they asserted, that in this way muriate of lime might be decomposed; and drew the conclusion that nascent hydrogen was not, as had been generally believed, the cause of the appearance of metals from metallic solutions."

"In 1805 various statements were made, both in Italy and England, respecting the generation of muriatic acid and fixed alkali from pure water. The fact was asserted by MM. Pachioni and Peele, and denied by Dr. Wallaston, M. Biot, and the Galvanic Society at Paris."

"It was in the beginning of 1806 that I attempted the solution of this question, and after some months labor, I presented to the Society the dissertation to which I have referred in the beginning of this lecture. Finding that acid and alkaline substances, even when existing in the most solid combinations, or in the smallest proportions in the hardest bodies, were elicited by voltaic electricity, I established that they were the result of decomposition, and not of composition or generation; and, referring to my experiments of 1800, 1801, and 1802, and to a number of new facts, which showed that inflammable substances, and oxygen, alkalies, and acids, and oxidable and noble metals were in electrical relation of positive and negative, I drew the conclusions that the combinations and decompositions by electricity were referable to the law of electrical attractions and repulsions."

It is curious that Davy should have overlooked the very early work of Van Marum.

From this work Davy naturally passed to the question of decomposing the fixed alkalies by the current. It is not so much to the work itself, beautiful as it was, to which I wish to direct attention now, as it is to the fact that Davy not only did a vast amount of work and secured wonderful results, but he also clearly pointed out the principles involved, and at this early date enunciated the conditions of successful operation upon which the modern practical applications of electric heat to metallurgical operations rest.

He has so plainly traced the history of his work and pointed out the underlying principles that I cannot do better than quote his own words. He says:[1]

"In the first attempt that I made on the decomposition of the fixed alkalies, I acted upon aqueous solutions of potash and soda, saturated at common temperatures by the highest electrical power that I could command, . . . though there was a high intensity of action, the water of the solutions alone was affected, and hydrogen and oxygen disengaged with the production of much heat and violent effervescence.

"The presence of water appearing thus to prevent any decomposition, I used potash in igneous fusion.

"By this arrangement some brilliant phenomena were produced.

"I tried several experiments on the electrization of potash rendered fluid by heat, with the hopes of being able to collect the combustible matter, but without success, and I only attained my object, by employing electricity as the common agent for fusion and decomposition."

Here is the clearest kind of statement of the value of using the current for the double purpose of fusing the material to be acted upon, and for decomposing it. In modern practice this principle was used, notably in the Heroult process of smelting aluminum alloys, and is now used in the successful processes of extracting pure aluminum, such as the Hall process in the United States and its equivalents abroad.

Continuing, Davy said:[2]

"The substance was likewise produced from potash fused by means of a lamp, in glass tubes confined by mercury and furnished with hermetically inserted platina wires by which the electrical action was transmitted."

This may be considered as a hint at electric heating under pressure, as proposed later by Werderman, de Grousilliers and Menges.

[1] Works of Sir Humphry Davy, 5, 58, 59, 60.
[2] Works of Sir Humphry Davy, 5, 61.

And in regard to the production of sodium he said:

"Soda, when acted upon in the same manner as potash, exhibited an analogous result; but the decomposition demanded greater intensity of action in the batteries, or the alkali was required to be in much thinner and smaller pieces."

In modern practice the benefits to be derived from alloying the separated metals, at the moment of their reduction, with another metal, is an essential element of the Cowles and Heroult aluminum alloy processes, and also of various processes of the electrolytic production of caustic soda, notably Castner's process. Here too Sir Humpry Davy was early in the field with both work and word.

After describing various obstacles and the conditions necessary in decomposing the alkaline earths as an essential to success, he says:[1]

"Or of combining them at the moment of their decomposition by electricity in metallic alloys, so as to obtain evidence of their nature and properties.

"Barytes, strontites and lime, slightly moistened, were electrified by iron wires under naphtha, by the same methods and with the same powers as those employed for the decomposition of the fixed alkalies.

"I had found in my researches upon potassium, that when a mixture of potash and the oxide of mercury, tin or lead was electrified in the Voltaic circuit, the decomposition was very rapid, and an amalgam or alloy of potassium was obtained; the attraction between the potassium and the common metals apparently accelerating the separation of the oxygen.

"The idea that a similar kind of action might assist the decomposition of the alkaline earths, induced me to electrify mixtures of these bodies and the oxide of tin, of iron, of lead, of silver, and of mercury, and these operations were far more satisfactory than any of the others.

"These experiments were made previous to April, 1808.

"The earths were slightly moistened, and mixed with one-third of oxide of mercury, the mixture was placed on a plate of platina, a cavity was made in the upper part of it to receive a globule of mercury, of from fifty to sixty grains in weight, the whole was covered by a film of naphtha, and the plate was made positive and the mercury negative, by the proper communication with the battery of 500.

"The amalgams obtained in this way were distilled in tubes of plate glass, or in some cases tubes of common glass."

In modern practice the crucible or containing vessel is usually

[1] Works of Sir Humphry Davy, 5, 104, 107, 108 111.

used as one of the electrodes, generally the negative. Sir Humphry Davy did the same, but like Siemens, made his crucible the positive pole, and in this particular case used external heat for fusing his charge. He says:[1]

"I fused a mixture of one part of silex and six of potash in a platina crucible, and preserved the mixture fluid, and in ignition over a fire of charcoal; the crucible was rendered positive from the battery of five hundred, and a rod of platina, rendered negative, was brought in contact with the alkaline menstruum.

"I tried similar experiments with mixtures of soda and alumina, and soda and zircone, and used iron as the negatively electrified metal."

The work of Sir Humphry Davy was followed by the work of Children, 1809–1815. In his first communication[2] he dealt mainly with the difference in the results produced by a battery consisting of a small number of large plates, and one consisting of a large number of small plates. The most interesting part of this paper, in tracing the history of metallurgical electric heating, is experiment 6, which is undoubtedly the first description of the passage of an electric current through a mixture of ore and resistance material, although it yielded no results. This principle was afterwards very successfully employed by the Messrs. Cowles. In this experiment of Children a mixture of sulphate of barium, red oxide of mercury and clay was submitted to the action of the current.

In his second paper[3] he described his work upon the relative conductivity of wires of various metals, and found that elevation of temperature affected the result.

He subjected various oxides, mostly of the rarer metals, to the action of the current, with varying results, some simply fused more or less, some were also reduced to metal. He also tried some experiments in simply melting.

His crucible consisted of a bit of boxwood charcoal, hollowed out on top with a little mercury in the cavity, serving as one electrode; upon this was placed a piece of the oxide; the other charcoal electrode was then brought near.

In this paper is also described Pepys celebrated experiment to determine that the diamond was really carbon. For this purpose a soft iron wire was bent and split by a saw; into the split some diamond powder was placed and bound in by fine wire, and the whole covered by leaves of talc. The current was then passed through the wire. The heat produced was not high, but the iron was carburized.

[1] Works of Sir Humphry Davy, 5, 119–120.
[2] Phil. Trans., 1809, 32.
[3] *Ibid.*, 1815, 363.

From this time on for over thirty years nothing seems to have been done in electric heating, although there were a few applications of the current to metallurgical processes in connection with external or other heat, such as the English Patents No. 9,946 of 1843, to A. Wall, for the use of the current in the blast furnace, and No. 10,362 of 1844, and No. 10,684 of 1845, to Napier for treating copper ore by the current in crucibles.

In 1848 and 1849 Despretz[1] published a series of articles in which he described the effect of combining the heat from three different sources, the electric current, the blowpipe and a burning glass. He clearly illustrates the difference between temperature and quantity of heat, the great difference there may be in the temperature of the source of heat and the temperature attained by the material heated, and that the loss of heat from the material heated, may be supplied by a source of heat at a comparatively lower temperature and allow a higher temperatured source of heat to exert its full heating effect. Thus on heating magnesia by the current at his command it simply became pasty, but on adding to this the heat of the burning glass it immediately volatilized in white fumes.

He determined that it is easier to volatilize carbon than to melt it; also that time, mgnesia and oxide of zinc behave in the same way. He melted alumina to a transparent glass; he also melted titanic acid in various forms, oxide of iron and disthen.

He suggested the use of the current for melting metals practically, and melted eighty grams of palladium and 250 grams of platinum.

In his last communication Despretz described an arrangement in which a quantity current was passed through his crucible while a separate series current was passed through the contents.

In 1853 an English patent No. 12,772 was granted to Staite & Petrie, in which the current was applied to the treatment and fusion of iridium.

In 1849 an English patent No. 5 was granted to Watson & Prosser for the use of the current in converting iron into steel by which the time of convertion was to be shortened, and the quality of the steel improved. In one case the current was passed through the enclosing trough, and in another the poles were put into the cementing material surrounding the bars. These propositions seem to resemble some of the modern ideas of producing heat, but it is not clear that Watson & Prosser used sufficient current to produce any considerable heating effect.

Although I have not yet been able to locate the exact date, I mention here the Grove furnace which has been called the pro-

[1] *Compt. Rend.* 28, 755; 29, 48,545, 709; 30, 369.

totype of the incandescent furnace. It consisted of a carbon crucible set in mercury, making the current connection, while the cover served as the other electrode. It was mentioned in La Lumiere Electrique, **19,** 350, and Scientific American Sup., April 24, 1886.

We come now to the first real attempt to employ the electric current to heat and act upon a charge of ore in a practical way. It is found in the invention of M. Pichon, patented in France, March 16, 1853, covered by English patent[1] No. 700 of 1853. In this process iron or other ores are mixed with carbon and shaken down between two or more pairs of electrodes through which the current is passing, when it melts, and after which it drops into an externally heated receptacle below.

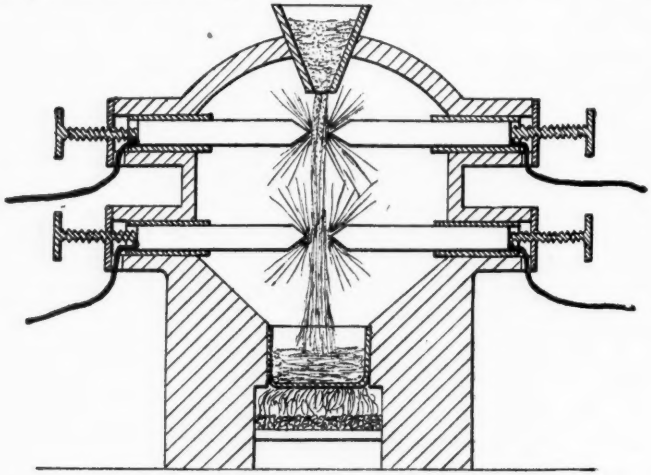


Fig. 1. Pichon's Furnace.

The description of this furnace (Fig. 1) in Practical Mechanics Journal speaks of the electrodes as being very large, but I think that feet should be read inches.

In 1854 Duvivier[2] placed a piece of disthen in the electric flame and produced globules of metal.

There is another long break after 1854 in our subject, strictly speaking, although there were many metallurgical propositions in which the current was employed, but they were either wet processes, or else flame heat was employed.

[1] See also *Practical Mechanics J.*, 6, 257, and Dingler, 131, 415.
[2] *Compt. Rend.*, **38,** 1066.

In 1866 Le Roux[1] published an exceedingly interesting and suggestive, but all too brief, communication upon the action of the arc upon lime and strontia. He decomposed lime and strontia in the arc and studied the reactions spectroscopically. He determined that the metals calcium and strontium were reduced, and carefully distinguished between the spectrum of the metals themselves and the spectrum of the white light resulting from the incandescence of the oxides. He asks the questions: Is the separation of the metals the result of electro-chemical decomposition? Is it due to vapor of carbon? Is it due to dissociation from heat alone? But he does not answer them.

We have seen that up to this time considerable work of a scientific character had been done from time to time in the field of dry electro-metallurgy, and that some suggestions at least had been made for the practical application of the current in this field. Undoubtedly, however, the cost of the current at this time was prohibitive. In looking over the field we can see the germs of modern processes, and easily imagine that if the early workers had been supplied with cheap current they would have carried their work very much farther, and developed practical electric metallurgical processes of value, but it remains as a fact that they did not have cheap current, and did not invent modern electric metallurgy.

With the development of the dynamo in the seventies came a wave of activity in the application of the current to metallurgy in the late seventies, and early eighties.

Before considering this growth in detail it is well to look at the advantages to be derived from the current as a heating agent. In doing this a sharp distinction between quantity of heat and degree of temperature should always be kept in mind. Unfortunately these terms are often used, even by persons who really know better, and who thereby mislead those who do not know better, as if they were synonymous. This is not at all the case. We may have an enormous quantity of heat developed at a low degree of temperature of which the pile of rotting apples is the old and familiar example. On the other hand, we may have a very high temperature developed by a small quantity of heat. A good blowpiper can melt fine platinum wire in a small blowpipe flame. While the combustion of a given quantity of fuel will always supply the same quantity of heat the temperature developed may vary enormously. When we carry this consideration farther and apply it to the practical application of heat, this for difference becomes much more marked and pronounced. For instance, a mixture of iron ore and carbon may be supplied with any quantity of heat at a low temperature without reduc-

[1] *Compt. Rend.*, 30, 1150.

ing the metal; or a mixture of bar iron and carbon may be heated indefinitely to a low temperature without producing steel, but once the proper degree of temperature is reached the required reactions take place. On the other hand, the proper temperature once attained, a sufficient quantity of heat at the right temperature must be supplied to carry on operations. While the good blowpiper can readily melt a fine platinum wire in his flame yet he cannot even soften a stout laboratory rod of platinum.

In practical work we are farther limited by materials of construction, their fusibility, their heat conduction and radiation.

The temperature attainable by ordinary combustion is limited by the temperature of dissociation of carbon and oxygen, which has been put at 2500° to 2600° C., but at such temperatures combustion is slow and losses of heat large, so that the practically attainable flame furnace temperature is probably about 1800° to 2000° C., while the practical oxyhydrogen blowpipe temperature may be several hundred degrees higher, but where the flame must not come in contact with the materials under treatment, and the heat must pass through the walls of crucible or muffle, we must be content with a very much lower temperature.

With the electric current the conditions are changed. The first and most striking factor is the enormous temperature that can be both experimentally and practically reached. What the maximum temperature attainable may be has not yet been established, but temperatures about 3800° C. have been measured by Moissan and Violle. The second factor is that the heat can be developed right at the point where it is utilized, and the losses reduced to the minimum. This is especially advantageous in replacing muffle and crucible heating, as is also the fact that the heat is secured without the introduction of enormous quantities of products of combustion. Again the temperature is under most perfect control, and can be adjusted with the utmost nicety. There are also minor advantages in the cleanliness and compactness of the operations.

It remains, however, that the cost of the current limits its practical application even now to a few special cases, and this is likely to remain so until the dream of the electrician of converting coal directly into current be realized.

In 1875 an English patent, No. 4,043, was issued to G. L. Fox for heating a crucible by the heat generated by resistance to the passage of the current, but curiously enough his resistance material was placed outside his crucible, and the heat had still to pass through the walls of the crucible.

In 1878 a voluminous French patent, No. 122,227, was issued

to M. Repieff, in which arrangements of electrodes for electric furnaces are shown. In the electric light part of his patent he also uses oxides to color his light.

In 1878 an English patent, No. 4,650, was issued to Clarke and Smith for producing ammonia by passing a mixture of nitrogen and hydrogen through sufficiently prolonged white heat produced by the electric arc

The next electric furnace was that described in the celebrated English patent, No. 2,110, of May 27th, 1879, to C. W. Siemens. This may be said to inaugurate the era of electric furnaces proper, and to be the first real hearty and systematic attempt to make practical use of heating by the current.

As described in the patent with all its attendants of water cooled electrodes and regulating devices it is a formidable and elaborate piece of apparatus, but divested of its accessories its real operating parts become simply a crucible provided with two electrodes, arranged either vertically (Fig. 2) or horizontally (Fig. 3), through which the current passes.

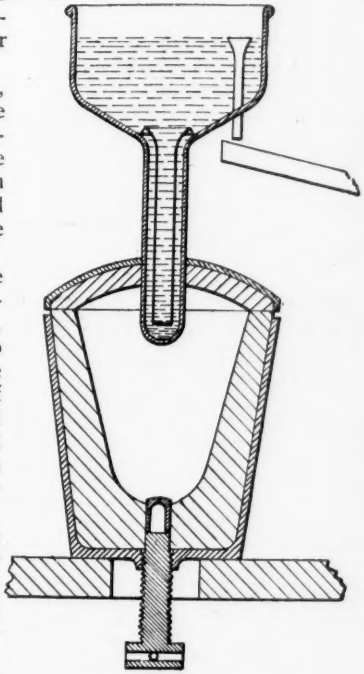


Fig. 2. Siemens' Furnace.

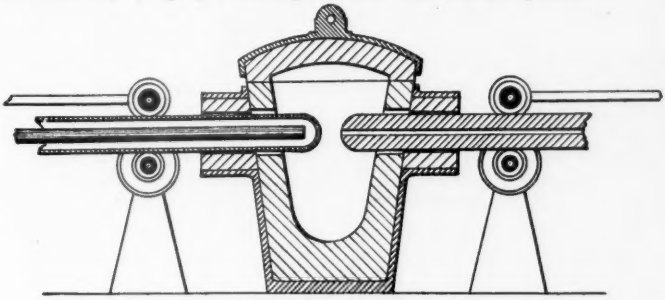


Fig. 3. Siemens' Furnace.

This apparatus was described and exhibited in actual operation before the Society of Telegraph Engineers[1] and the British Association.[2] The descriptions and exhibitions were confined for the most part to simple melting operations, although some attempts to saturate iron with carbon are described. It does not appear that Siemens ever used his furnace for the reduction of metals, although the article in *Iron* suggests that it might be so used. The death of Siemens undoubtedly cut off work in that direction with this apparatus.

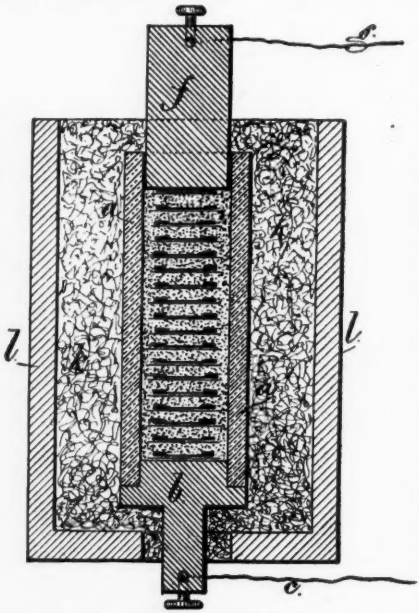


Fig. 4. Ball and Guest's Furnace.

In 1881 a United States patent, No. 236,478, was issued to Ball and Guest for an electrical carbonizing apparatus (Fig. 4) to produce carbons for the electric light. The articles to be carbonized are placed in a pile within a case and are surrounded by pulverized carbon. The case is then brought into the circuit and the contents thereby heated. A portion of the current passes through the carbon packing.

In 1881 an English patent, No. 304, was issued to Werdermann for preparing carbon from sugar, which was then subjected in a mold to a white heat by the passage of the current, for use in electric lamps. In the same year silicon was to be heated by the current to prepare it for use in electric lamps, French patent, No. 144,317.

The Belgian patent, No. 144,387, of Aug. 13, 1881, described a special form of furnace with one or more pairs of electrodes to be forced forward by springs. The furnace was calcined magnesia mixed with metallic oxides.

In the Engligh patent, No. 3,757, of 1882, Werdermann pro-

[1] *J. Soc. Tel. Eng.*, 9, 285.
[2] *Chem. News*, 46, 163; see also *Iron* Supplement, 1880, p. 424.

posed to heat silicon under pressure by the passage of the current.

At the Washington meeting of the American Institute of Mining Engineers, in February, 1882, in discussing the paper of Mr. Keith on the application of electricity to mining and

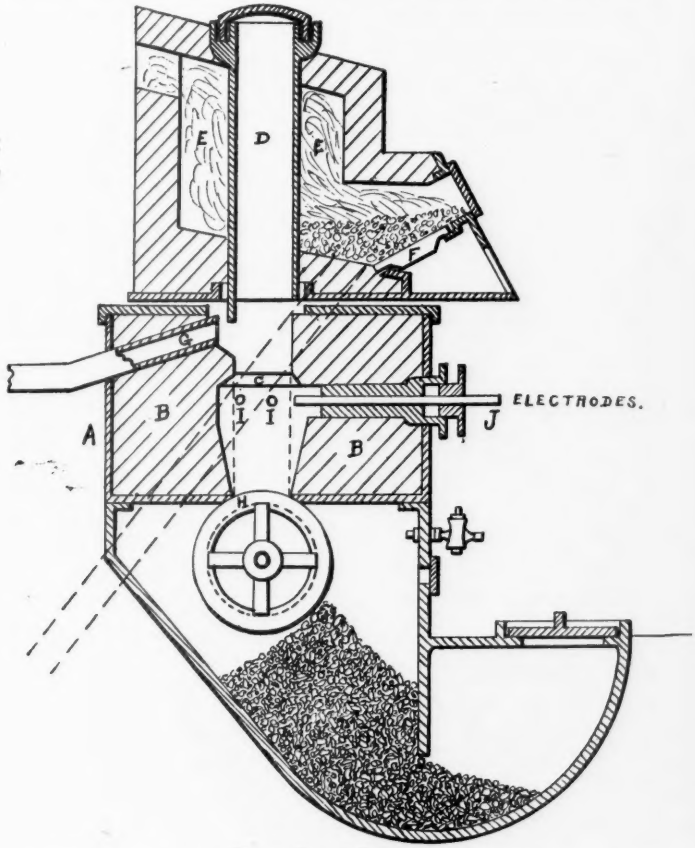


Fig. 5. Faure's Furnace.

metallurgy, Mr. H. M. Howe[1] briefly outlined a process which should have been developed into a successful commercial process. He said :

[1] Trans. Am. Inst. Min. Eng., 10, 317.

"The aluminous compound is placed in a carbon crucible, which is connected as the cathode of an electric current of great intensity. A voltaic arc is then thrown across from another electrode against this carbon crucible, the current thus first melting and then decomposing the aluminous compound, and metallic aluminum being deposited on the sides of the crucible."

In 1880–82–83–84 a series of patents[1] was issued to M. C. A. Faure, which has attracted considerable attention; more perhaps from their suggestiveness than from their actual contents. As described in the English patent, No. 6,058, of 1882, the process was designed for the reduction of sodium, and the furnace (Fig. 5) consisted of a tube in which the charge was first heated by an external fire. It was then passed into a chamber provided with electrodes for the passage of the current where it

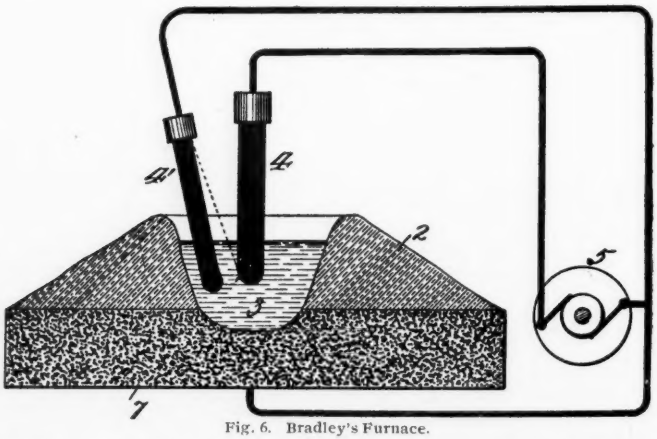


Fig. 6. Bradley's Furnace.

was intensely heated. Below was an automatic discharge for the refuse. There were also suitably condensing arrangements.

Chronologically considered, the United States patents to C. S. Bradley may be considered here, since the fundamental application was filed in February, 1883, although the patents were not issued for about nine years.[2] In these three patents (Fig. 6) the claims are drawn to cover three points. Using an unfused portion of the charge itself to enclose and contain the bath of fused material. Using the current for the double purpose of

[1] French patent No. 139,188. English patent No. 6,058, of 1882, and 5489 of 1883, and Belgian patent No. 63,385.

[2] United States patents, No. 464,933, of Dec. 8, 1891; No. 468,141, of Feb. 2, 1892, and No. 473,866, of 1892.

fusing and decomposing the charge. Using a downwardly projecting blowpipe, or other flame, to supply a portion of the heat.

A United States patent, No. 282,964, was issued to Delaplaine, Hendrickson, and Clamer, in 1883, for melting the tin off from tin scrap by the current.

When, in 1885–86, the simple and beautiful process of Messrs. E. H. and A. H. Cowles' was announced, both the scientific and practical worlds were surprised and intensely interested, and a revolution in high heat metallurgy seemed imminent, particularly in the metallurgy of aluminum, but later developments have not fulfilled the early promises in general metallurgy, and aluminum metallurgy has now passed out of the field of high heats.

This process consists in mixing the ore to be reduced with a so-called resistance material (which for practical reasons was carbon) and then passing the current through. The current generated a very high heat and difficultly reducible oxides were reduced to metal. In the case of aluminum the reaction went a step farther, and the reduced metal combined with the carbon and formed a carbide of aluminum.

The generation of the heat was attributed to the passage of the current through the resistance material. This was not altogether so, but the high heat was generated by the passage of the current from particles of the charge to other particles, in other words, by dividing up the current into innumerable small arcs, and the great advantage of the process lies in evenly distributing the heat of a large arc through a considerable space, through which the material to be acted upon is distributed.

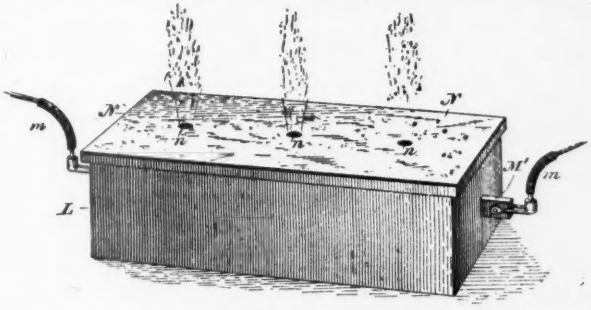


Fig. 7. Cowles' Furnace. (Outside).

The furnace (Fig. 7) consisted of an outside case of brick

[1] United States patents Nos. 319,795; 319,945; 324,658 and others. Also foreign patents. The Cowles process was widely described. Proc. A. A. A. S., **24**, 136; Trans. A. I. M. E., **14**, 492; *J. Franklin Inst.*, **121**, 111, and **122**, 51 and 273; *J. Soc. Chem. Ind.*, **5**, 206; *Mont. Sci.*, *1885*, p. 1288, and *1886*, p. 1032, Industries, Vol. 8, p. 273, 294, and elsewhere.

work, lined on the inside with carbon, then the charge containing the ore and carbon was put into the centre in contact with the electrodes, the charge was covered with carbon and a perforated cover placed over all.

By this process silicon, potassium, sodium, magnesium, calcium, chromiun, and titanium, as well as aluminum, were produced, but on account of so much of the aluminum combining with carbon, it became necessary to introduce an alloying metal

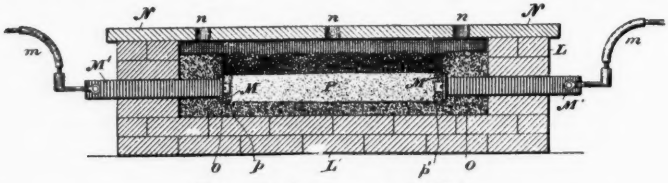


Fig. 7. Cowles' Furnace. (Inside).

into the charge. This was usually copper or iron. By this process the price of aluminum in alloys was very largely reduced, but no considerable amount of the pure metal was ever produced.

In 1886 a United States patent, No. 335,499, was issued to Bradley and Crocker, in which the current was used to heat the charge, and was divided into two portions, one part passed through the walls of the retort, and another passed through the charge.

In 1887–88 a series of patents[1] was granted to M. P. L. T. Heroult, in which alumina was melted by the passage of the current and then electrolyzed with molten copper, or iron, as the cathode with which the separated aluminum alloyed.

The furnace (Fig. 8) was a suitable containing vessel of carbon to which the negative wire was attached. The positive electrode was of carbon. In running the furnace copper or iron was first put in and melted by the current, then alumina was added, which was also melted, and then electrolyzed by the current. More alumina and copper, or iron, were added from time to time, and the resulting alloy was tapped out periodically.

This was a very promising high heat alloying process, but it, as well as the Cowles process, was superseded in the aluminum field by the Hall process of producing the pure metal, of which it is only necessary to say here that in this process the charge is both melted and electrolyzed by the current, but the fact is to be emphasized that only a comparatively low temperature is required.

[1] French patent No. 170,003. Belgian patent No. 77,100. English patent No. 7,426 of 1887. United States patent No. 387,876. See also Richards Aluminium, 2d ed., p. 36, and 309. Trans. A. I. M. E., **18**, 666. Industries, Vol. V, p. 405.

From 1892 to March 15, 1895,[1] there has been much published regarding the work of M. Henri Moissan, who has done so much fine work in the field of high temperatures, and has accomplished such wonderful results.

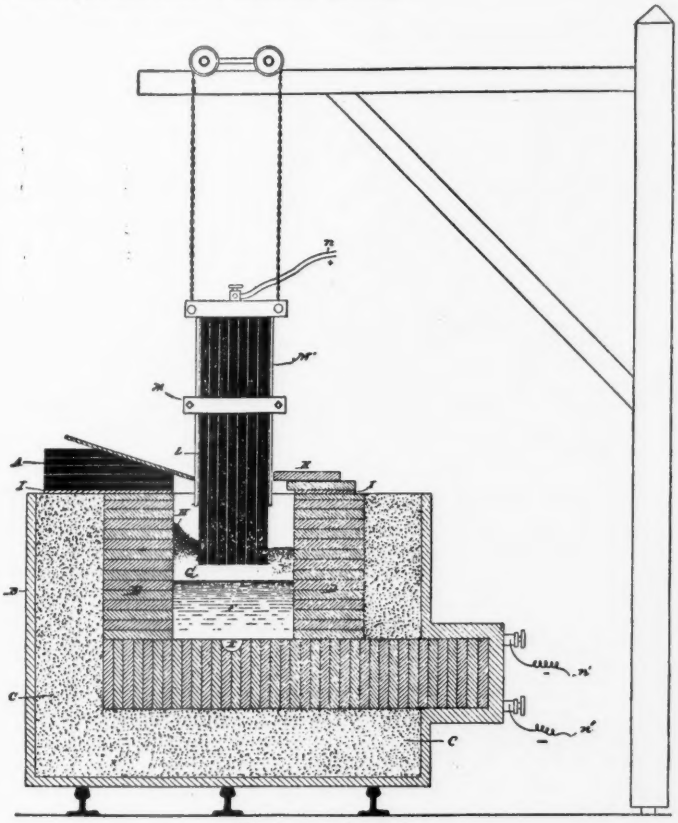


Fig. 8. Heroult's Furnace.

He employed various styles of furnaces and different amounts of current. His early furnace (Fig. 9) consisted of a simple block of quicklime suitably bound, and provided with electrodes

1 *Compt. rend.*, 115, 1031; 116, 549; 117, 679; 118, 116 and 501. La Nature, Vol. 21, pt. 1, *1893*, p. 225 and 275. *Ann. Chim. Phys.* [7], 4, 386.

and a cover. In this some very interesting results were obtained.

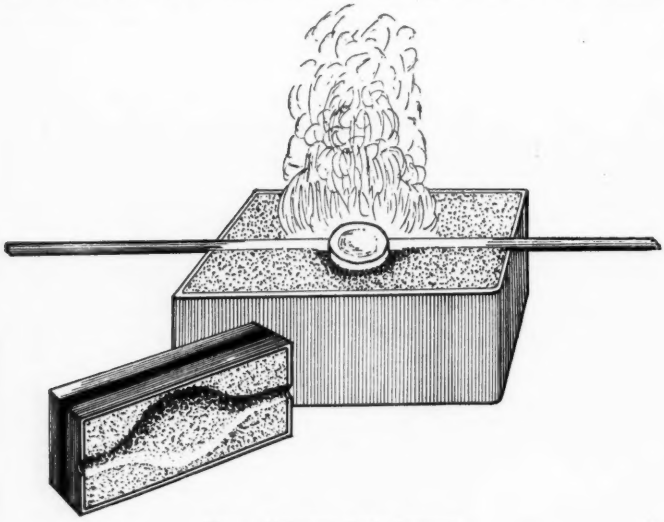


Fig. 9. Moissan's Early Furnace.

Another furnace (Fig. 10) was especially designed for determining the temperature by the specific heat method. A piece of carbon was

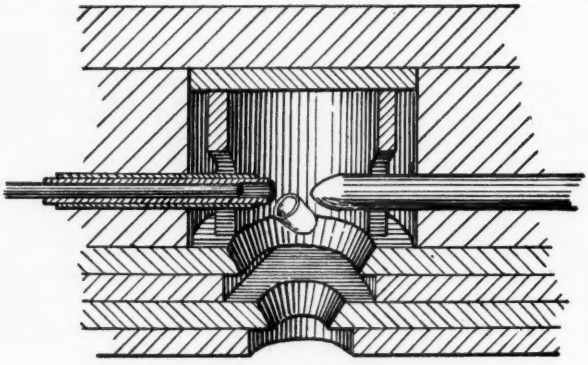


Fig. 10. Mossian's Specific Heat Furnace.

put on the end of one electrode, the current passed, and the carbon pushed off from the electrode, at the same time a slide was

withdrawn from the bottom of the furnace and the hot carbon allowed to fall in the calorimeter below. A number of temperature determinations were made in connection with M. Violle. Another furnace (Fig. 11) was provided with tubes for the intro-

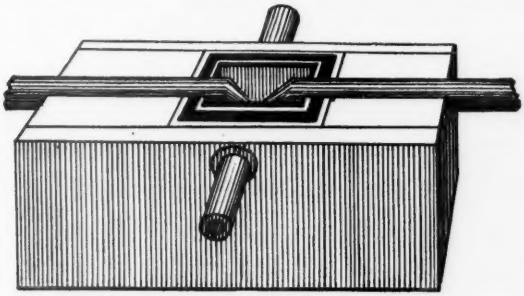


Fig. 11. Moissan's Furnace for Gas Reactions.

duction of gases. In this pure and colorless carbide of silicon was formed from carbon and silicon vapors. This furnace also had various layers, beginning with lime on the outside, and fol-

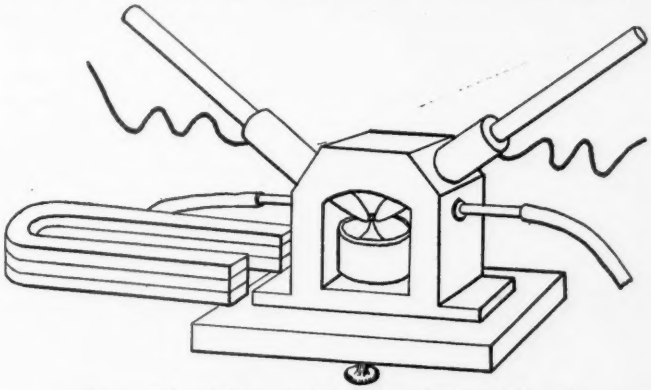


Fig. 12. Moissan's Furnace with Transparent Ends and Magnet.

lowed by carbon and then magnesia on the inside, or vice versa. Another furnace (Fig. 12) had transparent ends of glass, or mica, so that the operations could be watched. It also had magnets to direct and control the arc.

In this work Moissan designed to investigate and study the simple heating effect of the current separated as much as possi-

ble from any electrolytic effect. He speaks of and treats the arc as one would speak of an ordinary flame.

Moissan began with a very moderate current of thirty-five to forty amperes at fifty-five volts, and passed through various stages up to 1200–1600 amperes at 110 volts.

A few of the results obtained by Moissan may be mentioned. Magnesia was the only irreducible oxide found, it was melted and volatilized. Lime, strontia and magnesia began to volatilize before melting. Lime was easily melted and the metal calcium reduced, but it immediately combined with the carbon vapor forming calcium carbide (CaC_2). Alumina and platinum were volatilized. Artificial diamonds were produced. Various temperatures from 2000° to about 3800° C., were measured. Carbon begins to volatilize at about 3500° C. Various quantities of the rarer metals were reduced, 200 to 300 grams of uranium; 100 grams of vanadium; ten kilos of chromium, as well as manganese.

As in practical flame work the amount of fuel burned determines the temperature of the furnace, so in this case the amount of current passed determines the temperature and the furnace must be designed to stand the current to be employed. While Moissan's small furnace will stand the temperature developed by small currents, yet with 1200 amperes at 110 volts the lime and magnesia melts down, volatilize rapidly, and in a few moments the furnace is spoiled at a temperature of about 3500° C.

For materials of construction it was found that lime was the best nonconductor for heat, but its fusibility and the ease of forming the carbide, prevent its use for the inside of the furnace at very high temperatures. Compared with lime, carbon is a good conductor of heat. Magnesia is also a better heat conductor than lime. It does not form carbide of magnesium, and therefore can be heated very hot in direct contact with carbon, while lime cannot. It, however, is volatile, and can be melted at very high temperature. Practically, therefore, the outside of the furnace is quicklime, while the interior is variously lined with carbon or magnesia, or both, and when carbon is in direct contact with the lime it must not get too hot at the point of contact.

In 1893 a United States patent, No. 492,767,[1] was issued to E. G. Acheson, in which a mixture of silica, carbon, and salt was heated by the passage of the current and silicon carbide produced, which has found considerable application as an abrasive.

In the present early stage and activity of the calcium car-

[1] See also *J. Franklin Inst.*, **136**, 194 and 229; **137**, 401. Sci. Am., **70**, 215. West. Elec., **17**, 271. N. Y. Sun, Oct. 20, 1895. Cassiers Mag., **9**, 387.

bide and barium carbide questions it might not be wise to go into the details of the work and the claims of the various workers (Borscher, Maquenne, Moissan, Travers, Willson, I arrange these names simply alphabetically) but I mention these various carbide processes to show the present condition of our subject, and to draw special attention to a notable fact.

In reviewing our subject we find that in the early days the current was suggested, tried and used for various metallurgical operations, in which both the heating and decomposing actions of the current were utilized. Then in the principal, practical part of the field, that of the production of sodium and aluminum, the generation of intense temperatures became paramount. This activity culminated in the high heat processes of Cowles and Heroult, and they were very soon superseded by the low temperature processes of Hall for the production of aluminum, which carried with it the greater part of the demand for the production of sodium.

At the present day, therefore, there is no practical production of metals by high electric heats, with the possible exception of the production of chromium. On the other hand, high electric heats are being employed to go a step beyond the reduction of the metals, and to form new compounds, as in the carbide processes mentioned. In these the metals are first reduced, and are then immediately recombined with carbon, and thus in the field of high heat our subject becomes the application of high electric heat to chemistry.

Jan. 14, 1896. FREDERIC P. DEWEY.

NOTES.

The Second International Congress of Applied Chemistry.—The First International Congress of Applied Chemistry was held at Brussels, under the patronage of the Belgian Government, from August 4th to 11th, 1894. On the last day of the meeting it was voted to hold the next congress in Paris, in 1896. This approaching congress will be held in August of this year, the exact date to be hereafter published in this Journal, under the patronage of the French Government and pursuant to a plan of organization formulated by the Association of Chemists of the Sugar Industry and Distilling in France and the Colonies. M. Berthelot, the distinguished chemist, and now Minister of Foreign Affairs, is one of the Presidents of Honor. The congress will be held in ten sections, as follows:

Sec. I. Chemistry applied to the sugar industry.

Sec. II. Fermented and distilled beverages, cider, and vinegar.

Sec. III. Agricultural industries, including dairying, starch making, bread making, milling, etc.

Sec. IV. Agricultural chemistry, including fertilizers, soils, waters, cattle feeding, etc.

Sec. V. Chemistry applied to the customs, including methods of analysis of all the dutiable substances where the duty depends on chemical composition.

Sec. VI. Fats, tannin, rubber, paints, color, paper, etc.

Sec. VII. Photography.

Sec. VIII. Metallurgy.

Sec. IX. Biochemistry, foods, poisons, potable waters, microscopy, bacteriology, spectroscopy, etc.

Sec. X. Electrochemistry.

The undersigned committee for the United States has been appointed by the Provisional Council of the Congress, and we beg to call the attention of all American chemists, who expect to visit Europe during the coming summer, to the desirability of attending the meetings of the Congress. On application, the chairman of the committee will send a copy of the provisional program, showing the character of the questions which will be under discussion and containing a blank application for membership, which should be filled and sent to the proper address, before the date of the meeting. Already more than 900 chemists have entered their names as members of the Congress, and it is confidently expected that the membership will reach 2000. The committee respectfully invites the cooperation of all American chemists who hope to be able to attend the meetings or contribute papers for discussion.

Dr. H. W. Wiley, Dept. of Agriculture, Washington, D. C., Chairman.

Prof. Peter T. Austen, Polytechnic Institute, Brooklyn, N. Y.

Prof. F. W. Clarke, U. S. Geological Survey, Washington, D. C.

Dr. Charles B. Dudley, Pres. Amer. Chem. Society, Altoona, Pa.

Prof. F. A. Gooch, Yale University, New Haven, Conn.

Prof. Charles Loring Jackson, Harvard Univ., Cambridge, Mass.

Dr. Wm. McMurtrie, 106 Wall St., N. Y. City.

Prof. Charles E. Munroe, Columbian Univ. Washington, D.C.

Prof. Albert B. Prescott, Univ. of Michigan, Ann Arbor, Mich.

Prof. W. B. Rising, Univ. of Cal., Berkeley, Cal.

Dr. G. L. Spencer, Centralia, Wis.

Dr. W. C. Stubbs, Audubon Park, New Orleans, La.

Dr. Thomas Taylor, Washington, D. C.

The Cyanide Method of Extracting Gold from its Ores. Application to the Assays of Ores Poor in Gold and Silver.[1]*— Preliminary Notice.*—Having undertaken this work, at the suggestion of Prof. Mallet, only within the last two or three weeks, I have no exhaustive report of any nature to present. The work has not, as yet, advanced to such a stage that results can be stated satisfactorily in numbers. The attempts to apply this method to assay purposes *may* have been already made. If so, I have been unable to find any statement of that fact, and have no knowledge that such an attempt has been made.

I am at present comparing the method with the methods using chlorine and bromine. Quartz ores, too poor in gold or silver to be advantageously worked by the ordinary method of crucible assay, are the ores so far used.

The pulverized ore is well and repeatedly shaken with 0.25 per cent. solution of potassium cyanide, free access of air being provided for. After filtration and partial evaporation, the liquid is slowly passed over pure zinc filings. The zinc is then scorified with a larger amount of lead and the button cupelled.

The work has only progressed far enough to give hopes of good results. It seems at this stage to offer several advantages over the other methods mentioned.

The cyanide extracts the silver as well as the gold; bromine and chlorine only extracting the gold. The extremely disagreeable fumes of the other methods are entirely avoided. The work can be conducted without the use of hoods of fume rooms.

[1] Read at the Cleveland meeting, December 31, 1895.

The method yields the metals in a condition in which they can be more easily handled and their weights determined than can be the exceedingly fine precipitate from the bromine or chlorine solution.

The time is materially shortened, the long delay in the collection of the gold by the use of ferrous sulphate or oxalic acid being avoided.

In the few comparisons made, the amount of gold (and silver) extracted has been greater with the cyanide method than with the others. Though sufficient work has not as yet been done to make this reliable.

Before pronouncing on the availability of the method, other classes of ores than those so far used (quartz ore with and without pyrite) will be treated.

I expect to push the work as rapidly as possible.

Jan. 3, 1896. WILLIAM J. MARTIN, JR.

BOOKS RECEIVED.

Mining Journal of the Northwestern Mining Association. Spokane, Wash. 58 pp. Price 10 cents.

A Text-Book of Gas Manufacture for Students. By John Hornby, F.I.C. New York: Macmillan & Co., 1896. xiv + 216 pp. Price $1.50.

Bulletin No. 59. Spraying Experiments in 1895. Lexington, Ky.: Kentucky Agricultural Experiment Station of the State College of Kentucky. December, 1895. 19 pp.

Bulletin No. 60. Analyses of Commercial Fertilizers. I. Official Analyses. II. Analyses of Farmers' and Inspectors' Samples. Lexington, Ky: Kentucky Agricultural Experiment Station of the State College of Kentucky. December, 1895. 12 pp.